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Mossbauer Studies on Some Fe(III) Complexes

C. L. SHARMA,* ASHOK KUMAR SINGH and LAKSHMI DEVI

Chemistry Department, University of Roorkee, Roorkee (India)

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Mossbauer studies on Fe (imide)$_3$, [Fe (imide)$_3$ Am$_3$] and [Fe (imide)$_3$(en) (H$_2$O)] where imide=phthalimide or succinimide ion, Am=ammonia, methyl amine or ethyl amine, en=ethylenediamine have been carried out at 25±1°. The data have been correlated with the stereochemistry and / or magnetic properties of the complexes.

THERE is a pronounced difference in the structure of $FeCl_3.6H_2O$ and anhydrous $FeCl_3$[1] in their crystals. This difference is reflected in the Mossbauer spectra of these two forms[2,3]. It was considered worthwhile to study the M. B. spectra of a few iron(III) complexes wherein these chloride ions or water molecules are replaced by other large groups which are anionic or neutral in nature. With this in view Fe(Phthalimide)$_3$ and Fe(succinimide)$_3$ have been studied. Phthalimide and succinimide act as an anion after the imino hydrogen has been replaced. Coordination of the carbonyl is not favoured as that would involve the formation of unstable four membered ring. The compounds [Fe(Phthalimide)$_3$Am$_3$] and [Fe(succinimide)$_3$Am$_3$] where Am=ammonia, methyl amine or ethyl amine were also investigated. In these compounds three water molecules are replaced by three bulky anionic groups and three by amino groups. They are inner complex salts and hence their spectra were compared with [Fe(terpy.)$_3$Cl$_3$][4].

Experimental

Fe(Ph)$_3$, [Fe(Ph)$_3$Am$_3$] where Ph=Phthalimide, and [Fe(Ph)$_3$(en)H$_2$O] where en=ethylenediamine were prepared by the method reported earlier[5,6]. Fe(succ)$_3$, [Fe(succ)$_3$Am$_3$] where succ=succinimide and [Fe (succ)$_3$ (en)H$_2$O] were also similarly prepared. The composition and structure of all the above complexes were checked by chemical analysis, i.r., conductivity and magnetic measurements.

Mossbauer spectra of the complexes were recorded at 25±1° on a Mossbauer spectrometer using a 256-channel analyser and Kankeleit type constant acceleration drive[7]. The source used was~5 m Ci Co^{57} isotope in Palladium matrix. The calibration of the spectrometer was done by the peak positions of standard absorber Sodium Nitroprusside which were prepared by evenly spreading the samples on cellotape.

Chemical shifts δ (mm/sec.) and the quadrupole splittings △ E(mm/sec.) are given in table 1.

* 134/3 Vikas Nagar, University of Roorkee, Roorkee.

TABLE 1—CHEMICAL SHIFTS (δ) AND QUADRUPOLE SPLITTINGS (△E) AT 25°C WITH RESPECT TO SODIUM NITROPRUSSIDE ABSORBER.

Substance	δ(mm/sec)	△E(mm/sec.)
$FeCl_3$(ref. 3)	0.80 (−196°C)	—
Fe(phthalimide)$_3$	0.58±0.03	—
Fe(Succinide)$_3$	0.59±0.03	—
$FeCl_3.6H_2O$(ref. 2)	0.65 (−196°C)	0.50 (−196°C)
[Fe(terpy)Cl$_3$](ref. 4)	0.34	0.55
[Fe(imide)$_3$Am$_3$]	0.58±0.01	0.64±0.03
[Fe(imide)$_3$enH$_2$O]	0.55±0.03	0.69±0.03

imide=succinimide or phthalimide
Am =ammonia, methyl amine or ethyl amine.

Results and Discussion

[Fe(imide)$_3$] where imide=phthalimide or succinimide ion. In these complexes, the replacement of chloride ions by imide ions results in a decrease in isomer shift values indicating the greater electron density at the nucleus. No quadrupole splitting is observed because the symmetry of iron in these complexes remains the same as in anhydrous $FeCl_3$. As pointed out earlier, the imide ion does not function as a chelating agent.

In the complexes of the type [Fe(imide)$_3$Am$_3$], there is a decrease in isomer shift and increase in quadrupole splitting which again indicate the greater electron density at the nucleus in comparison to $FeCl_3$ $6H_2O$. No appreciable difference in the isomer shift of Fe(imide)$_3$ and [Fe(imide)$_3$Am$_3$] indicate that amines are very weakly coordinated to the metal. All the complexes are paramagnetic with a magnetic moment 5.8 B.M., characterised of high spin Fe(III) compounds.

[Fe(imide)$_3$(en) (H$_2$O)] complexes show a chemical shift (0.56 mm/sec) characteristic of spin free octahedral Fe(III), and the values are close to that observed

by Maddock et al[8]. Thus it may be concluded that the complexes are octahedral and the water molecule is coordinated to the iron ion.

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Physico-Chemical Investigation on the Complexes of Indium(III) with Ligands Containing Oxygen as Donor Atoms

R. SARIN and K. N. MUNSHI

Department of Chemistry, Nagpur University Campus, Nagpur.

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Potentiometric studies have been carried out on the complexes of indium (III) with acetylacetone, benzoylacetone, malonic acid and phthalic acid. The Calvin-Bjerrum *p*H-titration technique as used by Irving and Rossotti, has been applied to determine the stepwise formation constants of the complexes. The log K values have been computed by least squares method. The values of changes in △G, △H and △S accompanying complex formation have been evaluated at three different temperatures at an ionic strength 0.2*M* ($NaClO_4$). The results obtained indicate that if any anomalous change in the particular complex occurs due to steric or solvation factors then the effect due to these factors is reflected in the enthalpy and entropy changes associated with the metal-ligand coordination reactions.

ACETYLACETONE and benzoylacetone belong to a class of compounds known as β-diketones. A number of studies have been made on the β-diketones complexes formed with bivalent metal ions and rare earth elements.[1-6] Complex forming tendency of indium(III) with acetylacetone using extraction methods has also been reported.[7-8] Polarographic behaviour of indium(III) - acetylacetone has been studied by Cosovic and Branica[9]. Recently, the gas chromatographic behaviour of In(III) chelates with various β-diketones including benzoylacetone and acetylacetone has been reported by Utsunomlya.[10] Regarding dicarboxylic acids, Nair and Nancollas[11] were the first to communicate the thermodynamic parameters of ion association of some transition metal malonates. Equilibrium studies of complexes formed with malonic acid and phthalic acid have been reported by different group of workers[12-17]. However no reference is available on the potentiometric studies and thermodynamic characteristics of In(III) chelates formed with acetylacetone and benzoylacetone in 50% aqueous-dioxan media and with malonic acid and phthalic acid in aqueous media.

In the present communication are reported the "practical" proton-ligand stability constants and stepwise metal-ligand stability constants of above systems at various temperatures obtained by Calvin-Bjerrum titration techniques[18-19] as used by Irving and Rossotti[20]. The stepwise free energy changes (△G), enthalpy changes (△H) and entropy changes (△S) associated with the complex forming reactions have been evaluated at 25°, 35° and 45° in an ionic strength 0.2*M* ($NaClO_4$). The chelates formed with acetylacetone (ACA) and benzoylacetone (BNA) have been studied in 50% dioxan media whereas those formed with malonic acid (MLA) and phthalic acid (PTHA) have been studied in aqueous media.

The results obtained have been discussed in detail with reference to the results already reported in literature.

Experimental

Materials: Metal solution: A stock solution (0.02*M*) of In $(NO_3)_3.5H_2O$ (Schachardt, Munchen) was prepared in a calculated quantity of perchloric acid to prevent hydrolysis of metal ions. The metal content was estimated by precipitation of indium as 8-hydroxyquinolinate[21].

Ligand solutions: The stock solution (0.015*M*) of ACA (B.D.H.) was prepared both in double distilled water and in purified dioxan as the studies have been carried out in 100% water as well as in 50% dioxan-water media. The purity of ACA was checked by determining the refractive index (reported 1.45178; observed 1.4518). Due to the insolubility of BNA (Fluka) in water, the stock solution (0.015*M*) was prepared, in purified dioxan by direct weighing. MLA and PTHA both of B.D.H. make were used and their stock solution (0.02*M*) were prepared in double distilled water. The concentration was estimated by titrating a small portion of these solutions potentiometrically.

Sodium hydroxide-Sodium hydroxide (Merck) was dissolved in carbon dioxide free, doubly distilled water in a Pyrex vessel. The solution was kept overnight. A portion of the solution was diluted and its concentration was determined by titrating a portion of it potentiometrically against standard (0.1*M*) potassium hydrogen phthalate.

Sodium perchlorate: A solution of sodium perchlorate was prepared by dissolving AnalaR (Riedel) $NaClO_4.H_2O$ in doubly distilled water.

Perchloric acid : Analar sample (Merck) was diluted to prepare a stock solution (0.1*M*) which was titrated potentiometrically against standard sodium hydroxide solution to determine its concentration.

Dioxan : AnalaR (B.D.H.) dioxan was purified[22] before use, by refluxing it over excess of sodium for 6-12 hours and collecting the fraction distilling at 101-102°. The purity was ascertained by determining the refractive index which was found to be 1.439 against the reported value of 1.437 at 25°.

Apparatus : A *p*H-meter (Beckman model H-2) with a glass-calomel electrode assembly was used to determine the change in hydrogen ion concentration of the solution. The saturated calomel electrode was connected to the cell externally by means of agar bridge saturated with KNO_3 to prevent the formation of chloro complexes. The design of the cell was such that it allowed flushing of nitrogen (presaturated with solvent) through the solution and also enabled measurements to be carried out in an atmosphere of nitrogen.

metal complexes by this method, it is essential to have a prior knowledge of the "practical" proton-ligand stability constants. The values of $\bar{n}_A$ at various *p*H meter readings (B) were calculated from the acid and ligand titration curves. The equation (1) as used by Irving and Rossotti was employed :

$$\bar{n}_A = \left\{Y\, T^o_{CL} + \frac{(V' - V'')\,(N+E^o)}{(V^o+V')}\right\} \Big/ T^o_{CL} \qquad \ldots(1)$$

where V″ and V′ denote that volume of alkali added to reach the same value of *p*H (B) in the titration of ligand and acid respectively ; T^o_{CL} is the total ligand concentration, Y the number of replaceable protons attached to the ligand, N the normality of alkali, E^o the initial concentration of the free acid and $\bar{n}_A$ is the average number of protons attached per ligand ion.

The values of concentrations, V^o and Y used for these calculations for various ligands have been summarised in Table 1.

TABLE 1—VALUES OF CONCENTRATIONS ; V^o AND Y FOR VARIOUS LIGANDS

Ligand	V^o	Y	N	$E^o \times 10^3$	$T^o_{CL} \times 10^3$	$T^o_{CM} \times 10^3$
					Moles/litre	
ACA	75	1	1.020	1.014	5.219	1.067
ACA*	75	1	1.020	1.014	4.964	1.067
BNA*	75	1	1.020	1.014	5.168	1.067
MLA	100	2	1.020	1.035	4.947	1.045
PTHA	100	2	1.020	1.055	4.693	1.050

*experiments in 50% dioxan

Temperature was maintained by immersing the cell in an electrically maintained thermostat having a regulating accuracy of ± 0.2°.

Bjerrum-Calvin Titration : Three mixtures were prepared as follows : Mixture A : perchloric acid ; Mixture B : perchloric acid + ligand solution ; Mixture C : perchloric acid + ligand solution + metal solution, such that the concentrations of the common ingredients were identical in different cases. An appropriate amount of neutral sodium perchlorate was added to maintain the desired ionic strength. The volumes of the three mixtures were adjusted identical, using double distilled water or dioxan. The small contraction, during mixing, in the total volume of the solution was considered to be negligible for water-dioxan mixtures. The ratio between the metal salt and the ligands was such that, the maximum coordination number of the metal ion can be satisfied. A graph between *p*H-meter reading 'B' and the volume of alkali added was plotted. The three titration curves obtained were referred to as (A) acid titration curve, (B) ligand titration curve and (C) complex titration curve.

Results

"Practical" Proton-Ligand Stability Constants. : In order to calculate the formation constants of the

The calculation of the "practical" stability constants of the proton complexes was carried out by plotting a graph of $\bar{n}_A$ against *p*H (B) and then applying various computational methods[23].

The curves obtained from function $\bar{n}_A$ (B) were extended between 0 and 1 in the $\bar{n}_A$ scale for ACA and BNA indicating the dissociation of HACA and HBNA as follows :

$$HACA \rightleftharpoons ACA^- + H^+ \qquad \ldots (2)$$
$$HBNA \rightleftharpoons BNA^- + H^+ \qquad \ldots (3)$$

The formation curves for MLA and PTHA were found to be extended between 0 and 2 in the $\bar{n}_A$ scale indicating the dissociation of H_2MLA and H_2PTHA as follows :

$$H_2MLA \rightleftharpoons HMLA^- + H^+ \rightleftharpoons MLA^{-2} + H^+ \quad \ldots (4)$$

$$H_2PTHA \rightleftharpoons HPTHA^- + H^+ \rightleftharpoons PTHA^{-2} + H^+ \quad (5)$$

The values of log K^H (± 0.03) in case of ACA and BNA have been calculated by using two methods, (A) interpolation at half $\bar{n}_A$ value and (B) interpolation at various $\bar{n}_A$ values. In the calculation of log K^H_1 and

TABLE 2—"PRACTICAL" PROTON-LIGAND STABILITY CONSTANTS IN $\mu = 0.2M$ ($NaClO_4$)

Ligand	Constants	t=25° Method (A)	t=25° Method (B)	t=35° Method (A)	t=35° Method (B)	t=45° Method (A)	t=45° Method (B)
ACA	log K^H	8.97	8.98	8.88	8.88	8.78	8.78
ACA*	log K^H	9.55	9.55	9.48	9.48	9.41	9.41
BNA*	log K^H	9.80	9.80	9.70	9.71	9.63	9.62
MLA	log K_1^H	—	5.17	—	5.24	—	5.30
	log K_2^H	—	2.70	—	2.69	—	2.67
	log β^H	—	7.87	—	7.93	—	7.97
PTHA	log K_1^H	—	4.82	—	4.86	—	4.89
	log K_2^H	—	2.71	—	2.74	—	2.77
	log β^H	—	7.53	—	7.60	—	7.66

*experiments in 50% dioxan

log K_2^H for MLA and PTHA, the method of interpolation at various $\bar{n}_A$ values was employed. The values obtained at various temperatures and at $\mu = 0.2$ for all these ligands are summarised in Table 2.

Metal-Ligand Stability Constants : For a metal complex or chelate formation, taking place in steps in a homogenous solution, the step formation constants are given by equation (6)

$$Kn = C_{MLn}/C_{MLn-1} \cdot C_L \quad (n = 1,2,\ldots N) \qquad \ldots (6)$$

where Kn is called the nth metal-ligand stability constant.

In the present case the formation constants have been obtained by the analysis of the formation curves obtained by plotting $\bar{n}$ against pL. The value of $\bar{n}$ the average number of ligands attached per metal ion is calculated from the equation(7)

$$\bar{n} = (V''' - V'')(N + E^\circ)/(V^\circ + V')\ \bar{n}_A\ T^\circ_{CM} \qquad (7)$$

where T°_{CM} denotes the total concentration of metal present in solution and other terms have their usual meanings.

The free ligand exponent p^L has been calculated from equation (8)

$$p^L = \text{Log}\left[\left\{\sum_{n=o}^{n=j} {}^P\beta_n{}^H (1/\text{antilog B})(V^\circ + V''')\right\} \Big/ (T^\circ_{CL} - \bar{n}\ T^\circ_{CM})V_o\right] \qquad (8)$$

where ${}^P\beta_n{}^H$ is the overall "practical" proton-ligand stability constant.

It was observed in the complex forming systems of In(III) with ACA, BNA, MLA and PTHA that the metal titration curves did not join up parallel to the ligand titration curves indicating liberation of extra protons due to the hydrolysis of metal ions. Precipitation was observed for ACA in water media at pH 5.0, ACA in 50% dioxan media at pH 5.0, BNA at pH 5.0, MLA at pH 4.5 and PTHA at pH 3.8. Hence, in order to preclude errors due to hydrolysis in the calculation of $\bar{n}$, only the lower pH regions of titration curves were used. The $\bar{n}$ values used to calculate the stability constants of the complexes were not considered above pH ~4.0 in case of ACA and MLA complexes in water media, pH ~4.2 in case of ACA and BNA complexes in 50% dioxan media and 3.8 in case of PTHA complexes. The formation curves drawn

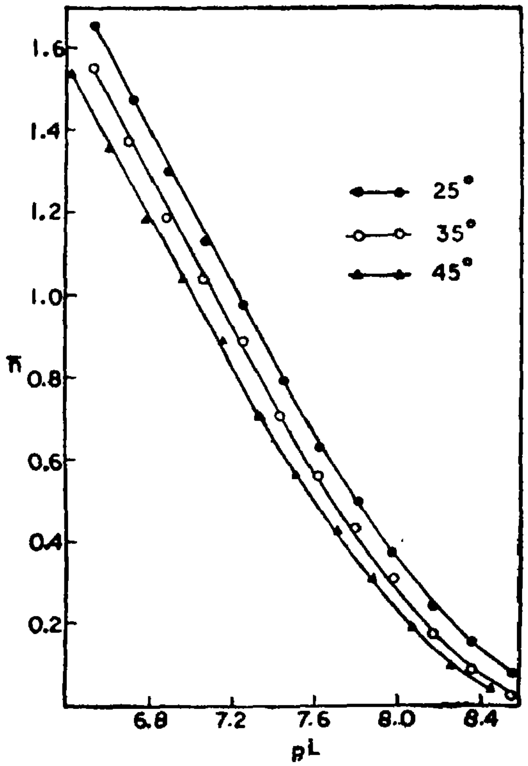


Fig. 1. Formation Curves of In(III)-ACA (aqueous) complex at ionic strength 0.2

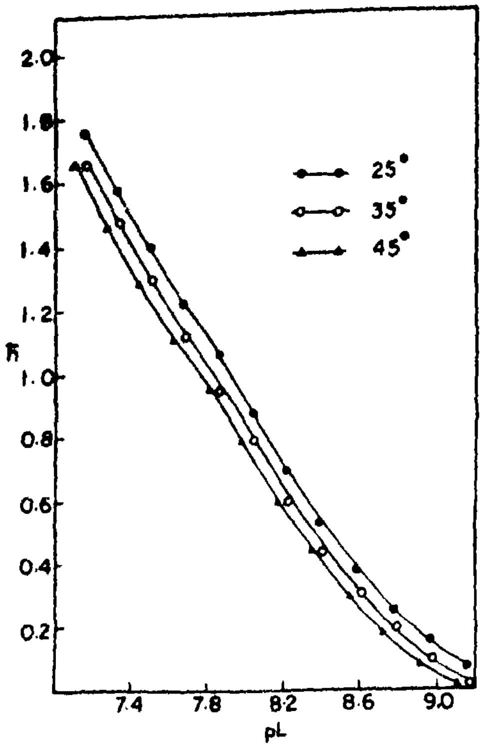


Fig. 2. Formation Curves of In(III)-ACA (dioxan) complex at ionic strength 0.2

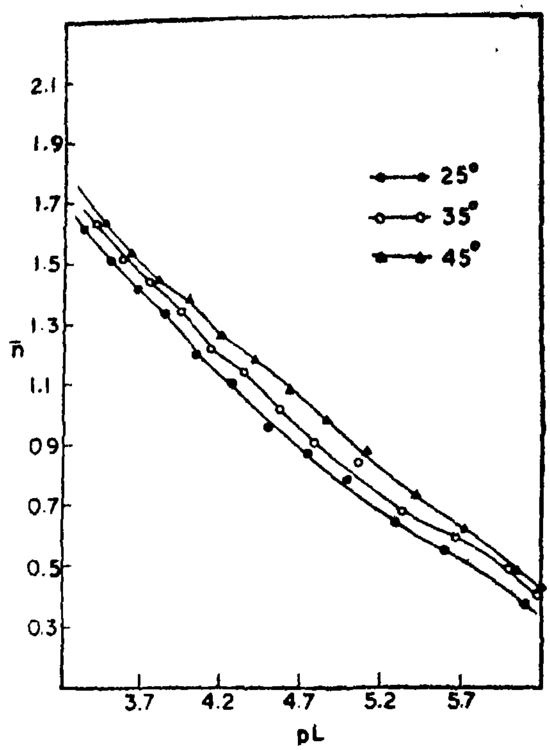


Fig. 4. Formation Curves of In(III)-MLA complex at ionic strength 0.2

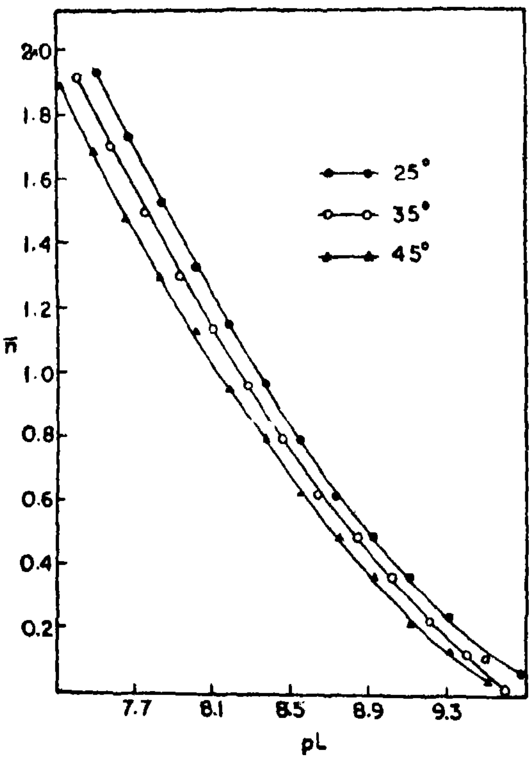


Fig. 3. Formation Curves of In(III)-BNA complex at ionic strength 0.2

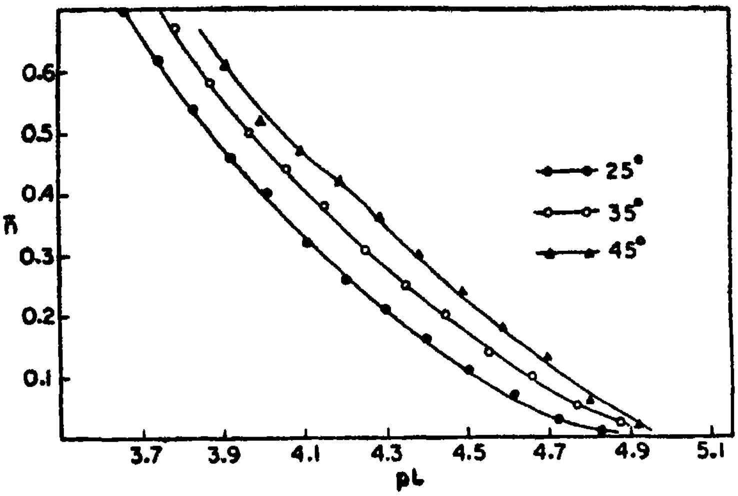


Fig. 5. Formation Curves of In(III)-PTHA complex at ionic strength 0.2

between $\bar{n}$ and pL for the complexes formed by In(III) with ACA in water (Fig. 1) ; ACA in dioxan (50%) (Fig, 2) ; BNA (Fig. 3) ; MLA (Fig. 4) are found to be extended between 0 and 2 in the $\bar{n}$ scale. In all these cases from the shapes of the formation curves it is apparent that the stepwise formation of complexes is not independent. Hence, the stability constants log K_1 and log K_2 have been calculated by the least squares method. The formation curves drawn between $\bar{n}$ and pL for the complexes formed by In(III) with PTHA are extending between 0 and 1 in the $\bar{n}$ scale (Fig. 5). Thus, the value of log K has been evaluated by the method of interpolation at half $\bar{n}$ value.

The values of log K_1 (± 0.03) and log K_2 (± 0.05) for the complexes formed by In(III) with ACA, BNA, MLA and PTHA at various temperatures and $\mu = 0.2$ are summarised in Table 3.

Thermodynamic Parameters: The values of the changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) have been calculated at three different temperatures and ionic strength $0.2M$ ($NaClO_4$) with the help of temperature coefficient and Gibbs-Helmholtz equation[24]. The equation (9) relating the stability constant to the free energy change of the reaction was employed for evaluting the value of the free energy change at various temperatures

$$\triangle G = -RT \ln k \qquad \ldots (9)$$

The value of the enthalpy change ($\triangle H$) has been determined from the slope of the curve obtained by plotting log K against $1/T$. This resulted in a straight line indicating that the assumption in the Gibbs-Helmholtz equation, that $\triangle H$ is constant at different temperatures is true. The value of the enthalpy change ($\triangle H$) was evaluated by equating the slope to $\cdot \triangle H/4.75$.

The entropy change ($\triangle S$) of the reaction was calculated at three different temperatures from the equation (10)

$$\triangle S = (\triangle H - \triangle G)/T \qquad \ldots (10)$$

The values of stepwise free energy changes ($\triangle G$), enthalpy changes ($\triangle H$), and entropy changes ($\triangle S$) calculated at three different temperatures viz. 25°, 35°, and 45° and $\mu = 0.2$ have been summarised in Table 4.

TABLE 3—METAL-LIGAND STABILITY CONSTANTS IN $\mu = 0.2$ ($NaClO_4$)

Complex	Constants	t = 25°	t = 35°	t = 45°
In(III)—ACA	log K_1	7.71	7.61	7.51
	log K_2	6.81	6.69	6.57
	log β	14.52	14.30	14.08
In(III)—ACA*	log K_1	8.30	8.22	8.14
	log K_2	7.55	7.46	7.38
	log β	15.85	15.68	15.52
In(III)—BNA*	log K_1	8.81	8.71	8.62
	log K_2	8.02	7.90	7.78
	log β	16.83	16.61	16.40
In(III)—MLA	log K_1	5.80	5.92	6.06
	log K_2	3.51	3.58	3.66
	log β	9.31	9.50	9.72
In(III)—PTHA	log K_1	3.87	3.96	4.03

*experiments in 50% dioxan media

TABLE 4—THERMODYNAMIC FUNCTIONS OF In(III) COMPLEXES AT μ=0.2

Complex	Reaction Step	Temp. °C	ΔG_n	ΔH_n	ΔS_n e.u.
			Kcal/mole		
In(III)—ACA	n=1	25	−10.52		
		35	−10.73	−4.0	+22
		45	−10.92		
	n=2	25	− 9.28		
		35	− 9.43	−4.9	+15
		45	− 9.56		
In(III)—ACA*	n=1	25	−11.14		
		35	−11.59	−3.2	+28
		45	−11.84		
	n=2	25	−10.29		
		35	−10.52	−3.7	+22
		45	−10.74		
In(III)—BNA*	n=1	25	−12.01		
		35	−12.27	−4.1	+27
		45	−12.54		
	n=2	25	−10.93		
		35	−11.13	−4.9	+20
		45	−11.32		
In(III)—MLA	n=1	25	− 7.91		
		35	− 8.34	+4.9	+43
		45	− 8.82		
	n=2	25	− 4.79		
		35	− 5.05	+3.3	+27
		45	− 5.32		
In(III) PTHA	n=1	25	− 5.28		
		35	− 5.58	+3.2	+28
		45	− 5.86		

*experiments in 50% dioxan

The precision of ΔG values is ± 0.05 K cal/mole for the first step and ± 0.08 Kcal/mole for the second step. The error limits of ΔH values are ± 0.5 Kcal/mole for the first step and ± 1.0 Kcal/mole for the subsequent steps. The ΔS values are having deviations of ± 2 cal/deg/mole for the first complex forming reaction and for the subsequent complexes the deviations are of the order of ± 3 cal/deg/mole.

Discussion

The nature of the formation curve for ACA in water and in dioxan + water medium is similar (Fig 1 and 2). Thus, it is reasonable to assume that the solvation sphere of metal ion and the metal complexes in 50% dioxan (which still contains more moles of water than of dioxan) is the same as that in water due to more polar nature of the water dipoles as compared to the dioxan dipoles and the low concentration of the solutes.

It is observed that the formation of indium(III) complexes of acetylacetone in 50% dioxan is accompanied by larger changes in entropy as compared to that in 100% water. The increased stability or free energy change for the formation of these complexes in dioxan + water medium arises as a result of difference in the standard states chosen for the two solutions and is due to a larger value of the entropy change, which more than compensates the decrease in the magnitude of -ΔH.

From the various relationships given between thermodynamic parameters and dielectric constant, the following general correlations can be obtained for the reactions,

$$In^{3+} + ACA^- \rightleftharpoons In(ACA)^{2+}$$

$$In(ACA)^{2+} + ACA^- \rightleftharpoons In(ACA)_2^+$$

1. ΔG has a negative sign and its magnitude will decrease as the dielectric constant of the medium decreases. Hence as shown in Table 4 the decrease in ΔG accompanying the formation of In $(ACA)_2^+$ in 50% dioxan medium is higher than that in 100% water medium

2. Δ S has a positive sign and its magnitude will increase with a decrease in the dielectric constant. If the "iceberg" concept of Evans and Frank[25] is applied to the dioxan + water medium, interaction between solvent dipoles and a metal ion will be of two types, (a) between those "frozen" water dipoles which are replaced by ligand molecules during complex formation, (b) between more distant water and dioxan dipoles which are oriented as a result of the electric field of the metal ions. For a metal complex dissolved in media of different dielectric constants, e.g. 100% water or 50% dioxan the interaction (a) will not change very much, a state of saturation will exist as far as the entropy changes are concerned. The "frozen" dipoles

contributing the solvation sphere of an ion consist entirely of the more polar water molecules ; but the effect due to (b) will cause much greater entropy change, on neutralisation of the charges on the cations and anions during complex formation in dioxan + water medium as compared to 100% water.

3. A lowering in the dielectric constant will increase the magnitude of the endothermic contribution. It may be seen from Table 4 that the exothermic heat of formation is lower in 50% dioxan than in water for the In(III)−ACA complexes.

The enthalpy changes accompanying the formation of BNA complexes of In(III) in 50% dioxan are more than ACA complexes. This is also the order of stability or the free energy change. The stepwise enthalpies of chelate formation $\triangle H_1$ and $\triangle H_2$ are equal (Table 4) within the limits of experimental error. This is in general agreement with the results reported in literature[26] and in agreement with the thermochemical cycle of Yatsimirskii and Grinberg[27]. Main contributing effect which remains constant is the difference between the heats of vaporisation of ligand and of displaced water. The only change is in the charge of the ion which will bring about a change in $\triangle S$.

It has also been shown by N.M.R. studies[28] that in benzoylacetone, the phenyl ring is coplanar with the hydrogen bonded enolic ring and hence it is able to increase the electron density on the adjacent oxygen atoms by resonance. These more basic donor oxygen atoms will therefore, form more covalent O-M bonds by virtue of their higher electron density and will lead to the greater negative values of $\triangle H$ for BNA complexes than ACA. This is consistent with the observed results of $\triangle H$.

It is also noted that the entropy changes for the formation of bisketonato In(III) complexes with ACA and BNA are constant to ±2 e.u. in the dioxan + water medium. This indicates that the stereochemical arrangement of the ligands around the In(III) ion for these complexes in dioxan + water medium is similar. The present results therefore, confirm the conclusions of Nakamoto et. al[29] who showed by I.R. studies that phenyl substitution increases the strength of O-M bond in the β-diketone complexes.

It is seen from the present results that the malonate complexes formed with In(III) are having greater stability than phthalate complexes. This may be due to the fact that latter involves less stable seven-membered chelate ring as compared to six-membered ring in case of former. The enthalpies of formation of metal dicarboxylate complexes involving malonate and phthalate ions are endothermic. In spite of these unfavourable enthalpy changes the complexes are stabilised by relatively large positive entropy change due to the liberation of water molecules from the ions accompanying complex formation.

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Formation Constants of Some Bivalent Metal Chelates of 2'-Hydroxy-4-Methoxy Chalcone

S. N. KAKKAR

Madhav Science College, Ujjain

and

P. V. KHADIKAR

School of Studies in Chemistry, Vikram University, Ujjain.

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The proton ligand formation constant of 2'-hydroxy-4-methoxy chalcone has been determined by spectrophotometric method. The mean value of PKa=11.40 is found to be in 60% (V/V) aqueous dioxane and 0.1*M* ionic strength ($NaClO_4$). The stepwise formation constants for 1 : 1 and 1 : 2 complexes of 2'-hydroxy-4-methoxy chalcone with Cu(II), Ni(II) and Co(II) has been determined using various computational methods employing *p*H metric technique in 60% (V/V) aqueous dioxane and 0.1*M* ionic strength ($NaClO_4$). The order of stability is found to be Co(II) > Cu(II) > Ni(II).

THE efficiency of chalcone as an analytical reagent for the spectrophotometric estimations of number of metal cations has been recognised[1,2]. Very few complexes of chalcones are, however, been studied employing potentiometric methods. Recently Khadikar et al.[3-7] have studied the chelate forming tendency of 2'-hydroxy and 2'-4'-dihydroxy-chalcones. In view of the usefulness of chalcones it would be of interest to study the chelating properties of other chalcones. The dissociation constant of 2'-hydroxy-4-methoxy chalcone and formation constants of its metal derivatives appear never to have been determined. In this communication such data are reported.

Experimental

2'-hydroxy-4-methoxy chalcone was prepared by the method described by Karrer et al[8]. (m.p. 92-93°) and were crystallised twice before use (Found C=75.44%, H=5.85%, Required C=75.59%, H=5.90%). All other chemicals used were of B.D.H. 'AnalaR' or equivalent quality. Since the chalcone is insoluble in water, dioxane-water mixture (60%V/V) was used as a solvent.

Standard solutions of the metal salts were prepared in double distilled water.

*p*H of the solutions were measured by using 'Polymetron Cl-41' *p*H meter with an accuracy of ±0.05 *p*H units.

Spectrophotometric measurements were done by using 'Bausch and Lomb' Spectronic 20' spectrophotometer.

Results and Discussion

The interaction M(II) with 2'-hydroxy-4-methoxy chalcone (HL) causes a considerable lowering in *p*H and a *p*H-metric titration of 1 : 1 metal : ligand system has revealed an inflection at one equivalent of alkali indicating thereby the replacement of one proton as a result of chelation. The chelation reaction may be represented as

$$M^{2+} + HL \rightleftharpoons ML^{+} + H^{+}$$

where M^{2+} stands for Cu(II), Ni(II) and Co(II).

*p*H metric titration of 1 : 2 and 1 : 3 mixtures of metal and ligand show inflection at two equivalents of alkali which corresponds to the formation of 1 : 2 complex in accordance with the reaction :

$$M^{2+} + 2HL \rightleftharpoons ML_2 + 2H^{+}.$$

The inflection at two equivalents of alkali for 1 : 2 and 1 : 3 metal : ligand *p*H-metric titrations indicates the absence of polynuclear species. The absence of polynuclear species finds further confirmation in the determination of formation constants in different metal ion concentration. The formation constants thence obtained did not differ more than 0.05 log units.

For calculating the stepwise formation constants, using Irving-Rossotti[10] method, the following solutions were prepared and total volume was made 50 ml.

(1) $HClO_4$ (0.4434*M*, 2.5 ml) + $NaClO_4$ (1*M*, 3.90 ml),

(2) $HClO_4$ (0.4434*M*, 2.5 ml) + $NaClO_4$(1*M*, 3.40 ml) + ligand (0.05*M*, 10 ml),

(3) $HClO_4$ (0.4434*M*, 2.5 ml)+$NaClO_4$ (1*M*, 3 20 ml) + ligand (0.05*M*, 10 ml) + metal salt solution (0.01*M*, 5 ml).

Calculated amount of dioxane and water is then added so that the medium is 60% (V/V) dioxane-water. The change in volume on mixing water and dioxane was determined by measuring the densities of the pure liquids and the mixtures as described by Irving and Rossotti[9]. The concentrations of the reactants were calculated with the allowance of this contraction and also for volume changes due to addition of alkali during the titration. Corrections for *p*H in aqueous-dioxane medium were made as described by Van Uitert and Haas[11]. The titrations were also carried out with half the metal concentration prescribed above, but the formation constants thence obtained did not differ more than 0.05 and 0.07 log units from those determined at the higher metal concentration. This suggests an absence of any polynuclear species under the experimental conditions used in the present investigation.

The ligand used is a very weak acid. The shifting of the absorption peak from 350 nm in acid medium to 375 nm in alkaline medium could be utilised for determining its p^ka value spectrophotometrically. Bower and Robinson method[9] using dioxane-water mixture (60% V/V) as solvent at 22° and ionic strength 0.1 *M* ($NaClO_4$) was used for the spectrophotometric determination of p^ka. The mean value of p^ka is found to be 11.40.

The stepwise formation constants of the complexes of the ligand with Cu(II), Ni(II) and Co(II) were determined employing Bjerrum-Calvin *pH*-titration technique as adopted by Irving and Rossotti[10]. A bulk electrolyte of 0.1 *M* sodium perchlorate was used to maintain constant ionic strength and reaction mixtures were all thermostated at 22±0.5°.

In calculating $\bar{n}$ and $p^{(L)}$ the concentrations were corrected for changes in volume produced by the addition of alkali during titrations. A series of values for $\bar{n}$ and $p^{(L)}$ corresponding to different B-values (*p*H-metric reading) were calculated using the equations given in an earlier paper[10].

The theoretical values of $\bar{n}$ have been calculated[13]. In calculating the theoretical values of $\bar{n}$ the corresponding values of log k_1 and log k_2 obtained by half-integral method were used.

The experimental and theoretical formation curves were obtained by plotting the corresponding values $\bar{n}$ against $p^{(L)}$. Both these formation curves did not differ within the experimental limit. The log k_1 and log k_2 were directly read from the formation curve using half-integral values of $\bar{n}$. In case of Co(II), $\bar{n}$, could not go beyond 1.099 and therefore the log k_2 values were determined from the $p^{(L)}$ at $\bar{n}$=1 as discussed by Bjerrum[14]. The refined values of log k_1 and log k_2 have also been determined by method of least square and simultaneous equations. The results show that the values obtained by all these three methods are in good agreement.

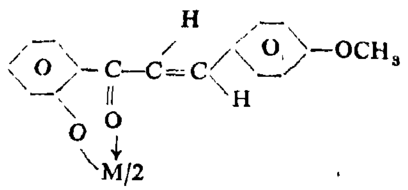
The mean values of log k_1, log k_2 and log β_2 along with log k_{av} and log k_1/k_2 are recorded in Table 1.

TABLE 1

	log K^*_1	log K^*_2	log $^*\beta_2$	log K^*_{av}	log K_1/K_2
Cu(II)	8.50	7.28	15.78	7.89	1.22
Ni(II)	5.63	4.56	10.20	5.10	1.07
Co(II)	8.77	7.50	16.27	8.13	1.23

* Mean values.

One would expect a bigger difference between log k_1 and log k_2 values in such ligands because of possible steric hindrance to the linking of the second lingand to the metal ion. The smaller difference may be due to trans structure (I) :



(I)

As normally encountered, the average formation constants, log k_{av} (Table 1) are consistently lower than log $p^{k^H_1}$ (proton ligand formation constant) of 2′-hydroxy-4-methoxy-chalcone. The perusal of Table 1 shows that the ratio log k_1/k_2 is positive in all cases. Separation factors between first and second formation constants are well within the expected range and the absence of high values implies there is little or no steric hindrance to the addition of the second ligand molecule. This is in favour of the assignment of trans-structure(I).

Also, it is apparently indicated that there is almost equal tendency for the formation of neutral complex species ML_2 as for species ML . Further, it is observed that the values of log k_2 are lower than log k_1 by 1.02-1.27 units. This suggests that in these systems not only the statistical effect (which gives the value of log k_1 − log k_2=0.60 units) should be considered but the electrostatic effect also becomes important[15].

It will be interesting to compare the values of protonation constants and formation constants of 2′-hydroxy-4-methoxy-chalcone with the corresponding values of 2′-hydroxy-and 2′, 4′-dihydroxy-chalcones reported by us[8,7]. The values of above mentioned constants are lower than those of 2′-hydroxy-and 2′, 4′-dihydroxy-chalcones. This greater stability of 2′-hydroxy-and 2′, 4′-dihydroxy chalcone complexes may

be attributed to the greater tendency of resonating structure for them as compared to 2'-hydroxy-4-methoxy-chalcone.

The perusal of Table 1 shows that the stability order is Co(II) > Cu(II) > Ni(II). This order of stability follows neither the Irving-Williams' rule nor any of the empirical orders reviewed by Irving and William[12].

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Rare Earth Complexes of Some Amino Acids : A Potentiometric Study

SANTOSH D. MAKHIJANI and SATENDRA P. SANGAL*

Laxminarayan Institute of Technology, Nagpur University, Nagpur

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Stability constants of 1 : 1 complexes of Sc(III), Y(III), La(III), Ce(III), Pr(III) and Nd(III) with Glycine, Asparagine and Glutamine at 30°, at an ionic strength of 0.2 *M* $NaClO_4$ have been determined by Irving-Rossotti *p*H-titration technique. Free energies of the above said complexes are also reported. The trend of stability constants irrespective of amino acids under investigation is found to be Sc(III) > Y(III) > Nd(III) > Pr(III) > Ce(III) > La(III). In terms of amino acids, the stability constants of any particular rare earth ion decreased in order Glycine > Glutamine > Asparagine.

EXTENSIVE work has been reported on metal chelates of amino acids with various metal ions. But, so as to obtain the trend and values of stability constants of the complexes of rare earths with amino acids in terms of metal ions as well as amino acids, it was proposed to study the complexes of some rare earths with various amino acids containing different substituent groups. The metal ions selected for study are Sc(III), Y(III), La(III), Ce(III), Pr(III), and Nd(III) and amino acids are Glycine, Asparagine and Glutamine. The studies include the determination of "Practical" proton-ligand and metal-ligand stability constants at 30°, at an ionic strength of 0.2 *M* $NaClO_4$. The stability constants are obtained by the method of Bjerrum-Calvin *p*H-titration technique[1,2] as used by Irving and Rossotti[3]. The free energy changes accompanying the equilibrium are also reported.

Experimental

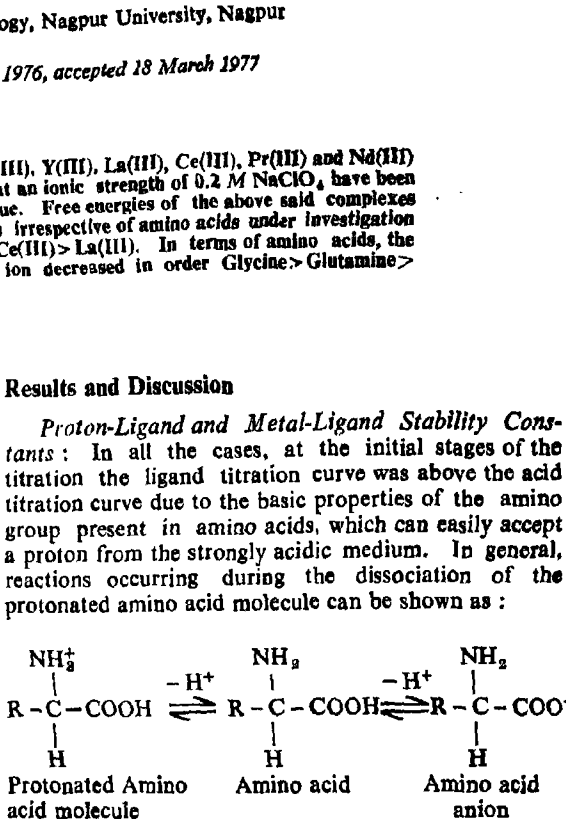
Chemicals : Stock solutions of 0.01 *M* Glycine (E. Merk, Germany), Glutamine (BDH, made in England) and Asparagine (Reanal, Hungary) were prepared in carbon dioxide free double distilled water. The metal solutions were prepared by converting oxides into perchlorates in usual manner. These solutions were standardized by EDTA method[4]. Perchloric acid (0.1 *M*, A. R. Merck), sodium hydroxide (approx. 1 *M*), potassium hydrogen phthalate (0.05 *M*, BDH) and sodium perchlorate (1 *M*) (all analytical reagents) were prepared in carbon dioxide free double distilled water. Sodium hydroxide was standardized with potassium hydrogen phthalate. potentiometrically.

Apparatus : A *p*H-meter with a combined glass calomel electrode was used for *p*H-measurements. The nitrogen gas was passed continuously during the course of titration. The cell was immersed in an electronically operated thermostat having an accuracy of ±0.1° and also, the contents of the cell were stirred continuously during the titrations.

* Senior Author

Results and Discussion

Proton-Ligand and Metal-Ligand Stability Constants : In all the cases, at the initial stages of the titration the ligand titration curve was above the acid titration curve due to the basic properties of the amino group present in amino acids, which can easily accept a proton from the strongly acidic medium. In general, reactions occurring during the dissociation of the protonated amino acid molecule can be shown as :



The "Practical" proton-ligand and metal-ligand stability constants were obtained by usual equations as in previous communications[5,6]. The values of proton ligand and metal ligand (1 : 1) stability constants so obtained by using half $\bar{n}$-values methods are tabulated in Table 1.

TABLE 1—PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS AT 30°, AT AN IONIC STRENGTH OF 0.2*M* $NaClO_4$.

Metal	Constant	Amino Acid Glycine	Glutamine	Asparagine
	$\log K_1^H$	9.225	8.815	8.555
H^+	$\log K_2^H$	2.250	2.210	2.085
	$\log \beta^H$	11.475	11.025	10.640
Sc(III)	$\log K_1$	7.749	7.405	7.083
Y(III)	$\log K_1$	5.055	4.720	4.425
La(III)	$\log K_1$	3.850	3.710	3.525
Ce(III)	$\log K_1$	4.455	3.945	3.775
Pr(III)	$\log K_1$	4.500	4.275	4.085
Nd(III)	$\log K_1$	4.615	4.530	4.260

Precipitation was observed in all the cases, and hence calculations were done only in pH-range where there was no precipitation. The precipitation may be due to the hydroxo complex formation, which can be explained in the following manner :

$$M^{3+} + AA^- \rightleftharpoons (M.AA)^{2+} \quad (1)$$

$$(M.AA)^{2+} + 2OH^- \rightleftharpoons [(M.AA)(OH)_2]\downarrow \quad (2)$$

(where AA = amino acid)

Free Energies : The Gibbs-Helmholtz equation[7] has been used to obtain the free energy changes ($\triangle G$) of the reactions. The total free energy change is given by equation

$$\triangle G = -RT \ln \beta \quad (3)$$

where β is the overall stability constant. The values of free energies so obtained are tabulated in Table 2.

TABLE 2—FREE ENERGIES OF THE COMPLEXES OF RARE EARTH IONS WITH AMINO ACIDS AT 30°C (μ = 0.2 M $NaClO_4$).

Metal	Glycine	Glutamine	Asparagine
H^+	−16.015	−15.386	−14.849
Sc(III)	−10.815	−10.334	− 9.885
Y(III)	− 7.055	− 6.587	− 6.176
La(III)	− 5.373	− 5.178	− 4.920
Ce(III)	− 6.217	− 5.506	− 5.268
Pr(III)	− 6.280	− 5.966	− 5.701
Nd(III)	− 6.441	− 6.322	− 5.945

From Table 1 it can be seen that the trend of stability constants for all the amino acids under investigation is same i.e. Sc(III) > Y(III) > Nd(III) > Pr(III) > Ce(III) > La(III). Thus, the statement "stability increases with the decrease in ionic radii" is proved in the present case also. Table 1 also reveals that, proton-ligand as well as metal-ligand stability constants of the amino acids follow the same order Glycine > Glutamine > Asparagine.

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Ion-Exchange Study of Manganese(III) Pyrophosphate

S. P. MALLELA and B. L. KHANDELWAL

Department of Chemistry, Indian Institute of Technology, New Delhi-110029

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Manganese(III) pyrophosphate can be isolated from manganese(II), cobalt(II), nickel(II), copper(II) and selenium(IV) by passing through an anion exchanger De Acidite FF at pH$\approx$2.5 and eluting it out by 1M tetra potassium pyrophosphate at pH$\approx$6. The distribution coefficient has been determined. The effect of pH and concentration of tetrapotassium pyrophosphate on the elution of manganese(III) pyrophosphate has also been studied.

MANGANESE(III) compounds are strong oxidants and their stability depends upon the presence of complexing agents e. g. sulphate, fluoride or pyrophosphate[1]. Manganese(III) pyrophosphate[2,3,4] is stable over long periods and has been used as oxidant in visual, potentiometric and spectrophotometric titrations. Recently Bogdanovich[5] et al have made a detailed study of the composition and stability of manganese(III) pyrophosphate. The present study describes an investigation of the ion exchange behaviour of manganese(III) pyrophosphate and its separation from manganese(II), cobalt(II), nickel(II), copper(II) and selenium(IV).

Experimental

All the chemicals used were of E. Merck's guaranteed reagent grade. Double distilled water was used throughout the experiments. The anion exchange resin used was of Permutit's De Acidite FF in sulphate form (20-50 mesh). Manganese(III) pyrophosphate was prepared following Belcher and West[2] method and standardised spectrophotometrically with standard arsenic(III) solution. pH values were adjusted by means of dil. KOH/dil. H_2SO_4.

The ion exchange column used was made of a glass tube of 10 mm diameter with a tap funnel at the top and glass wool at the bottom to support the resin bed. The bottom of the column was drawn to a narrow diameter and bent in double U shape so that the outlet was slightly higher than the top of the resin bed. The column was filled with 1.5g of air dried resin. Unicam SP 700A Spectrophotometer and Bausch & Lomb's Spectronic 20 were used for the absorbance measurements. Elico pH meter (Model LI-10) was used for pH measurements.

Determination of q and K_d

1g samples of the air dried resin were equilibrated for an hour with 20 ml solution of manganese(III) pyrophosphate at various pH values. The fraction of manganese(III) remained in the solution after equilibrium was determined spectrophotometrically[6]. Knowing the initial and the equilibrium concentrations of the manganese(III) in the external solution, the amount, q, sorbed per 1g of the exchange material was calculated. K_d, the distribution coefficient values were calculated by the relation[7]

$$K_d = \frac{\text{Amount of Mn(III) in the resin}}{\text{Amount of Mn(III) in solution}} \times \frac{\text{ml, solution}}{\text{g, dry resin}}$$

The results are given in Table 1 and 2.

Elution Curves of Manganese(III) Pyrophosphate : 10 ml of 7.3×10^{-3} M manganese(III) pyrophosphate solution at pH 2.5 was added to the column. The adsorbed species was then eluted with tetra potassium pyrophosphate of known concentration and pH value. The effluent was collected in fractions of 5 ml and each was analysed for the manganese(III). The concentration of manganese(III) was then plotted against the volume of effluent collected (Fig. 1 and 2).

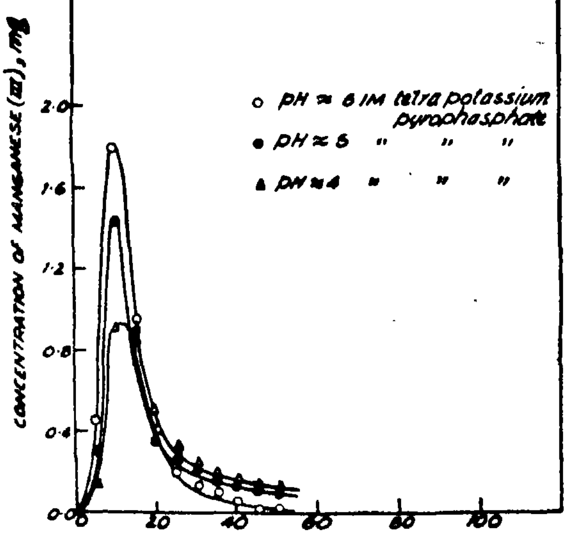


Fig. 1. Effect of pH of tetra potassium pyrophosphate on the elution of manganese (III) pyrophosphate.

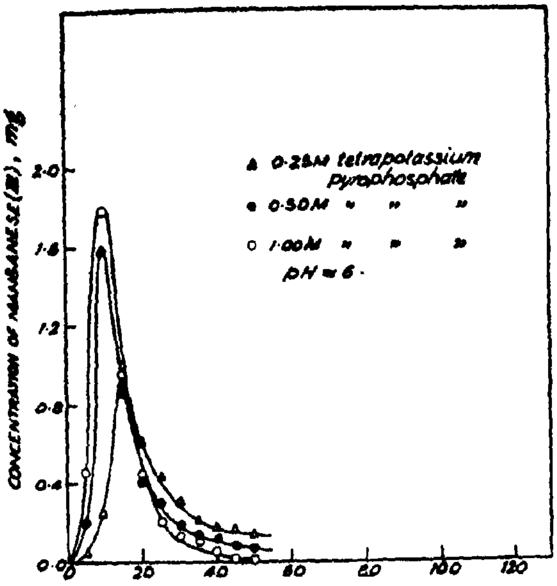


Fig. 2. Effect of concentration of tetra posassium pyrophosphate on elution of manganese (III) pyrophosphate.

Separation of Manganese(III) Pyrophosphate

The column was thoroughly washed with 1% H_2SO_4. Manganese(III) pyrophosphate solutions containing one of the foreign ions like manganese(II), cobalt(II), nickel(II), copper(II) and selenium(IV) were passed through the column at *p*H 2.5 with a flow rate of 0.25 ml per minute. Manganese(III) was fixed on the resin as $[Mn(H_2P_2O_7)_3]^{-3}$ leaving other ions in the effluent. The effluents were analysed by standard methods. Manganese(III) pyrophosphate was eluted with 50 ml of 1*M* tetrapotassium pyrophosphate at *p*H 6 with a flow rate of 0.75 – 1.50 ml per minute.

Results and Discussion

The dependence of q and K_d values on *p*H has been shown in Table 1. The K_d value increases as the *p*H changes from 1.0 to 2.5 and then becomes almost constant upto *p*H 6. This is in consistent with the dissociation constant values of pyrophosphoric acid[8] (pK_1 = 0.85, pK_2 = 1.96, pK_3 = 6.54 and pK_4 = 8.44). However, the slight decrease of K_d when *p*H is increased to 6 is possibly because of the preferential sorption of the free pyrophosphate on the resin.

Table 2 shows the effect of manganese(III) pyrophosphate concentration on q and K_d values. The decrease in K_d values at higher concentrations of manganese(III) pyrophosphate is due to the over loading on the resin. The constancy of K_d at different ratios of volume of solution to mass of resin is shown in Table 3.

TABLE 1—DEPENDENCE OF q and K_d VALUES OF MANGANESE(III) PYROPHOSPHATE ON *p*H.

Amount of the exchanger = 1g | Total volume = 20 ml | Temp = 26°C

*p*H	Amount of manganese (III) mg. Before equilibrium	After equilibrium	q/1g m-equiv.	K_d
1.0	12.09	6.32	0.32	18.26
1.5	12.09	5.57	0.35	23.41
2.0	12.09	4.91	0.39	29.25
2.5	12.95	4.96	0.44	32.22
3.0	12.09	4.69	0.40	31.55
4.0	12.09	4.69	0.40	31.55
5.0	12.10	4.90	0.39	29.39
6.0	12.10	5.10	0.38	27.45

TABLE 2—DEPENDENCE OF q & K_d VALUES OF MANGANESE(III) PYROPHOSPHATE ON THE CONCENTRATION OF MANGANESE (III).

Amount of the exchanger = 1g | Total volume = 20 ml | *p*H = 2.5 | Temp = 26°C

Amount of manganese (III), mg Before equilibrium	After equilibrium	q/1g m-equiv	K_d
11.77	4.69	0.39	30.19
12.95	4.96	0.44	32.22
14.95	5.89	0.49	30.76
17.66	8.01	0.53	24.09
21.00	11.50	0.52	16.52
24.00	14.28	0.53	13.61

TABLE 3—DEPENDENCE OF q AND K_d VALUES ON MASS OF THE RESIN AND VOLUME OF THE SOLUTION.

*p*H = 2.5 | Temp = 26°C

Amount of the resin, g	Amount of manganese(III), mg Before equilibrium	After equilibrium	Total Vol. ml	q/1g m-equiv.	K_d
0.50	12.00	8.00	30	0.44	30.00
0.75	14.95	7.75	25	0.52	30.97
1.00	14.95	5.89	20	0.49	30.76
1.50	24.00	9.50	30	0.53	30.53
2.00	26.00	6.60	20	0.53	29.40

TABLE 4—SEPARATION OF MANGANESE(III) PYROPHOSPHATE FROM ADDED FOREIGN IONS.

Amount of the exchanger = 1.5 g | *p*H = 2.5

Foreign ion	Foreign ion mg added,	Manganese(III) present, mg	Foreign ion recovered, mg	Manganese(III) recovered, mg
Mn(II)	27.69	1.16	27.67	1.16
	5.54	0.29	5.54	0.29
Co(II)	10.03	1.16	10.02	1.16
	2.01	5.44	2.00	5.43
Ni(II)	23.60	4.36	23.58	4.36
	5.60	2.18	5.59	2.17
Cu(II)	32.09	7.97	32.06	7.95
	12.84	3.22	12.82	3.21
Se(IV)	12.58	7.97	12.57	7.97
	2.29	3.99	2.28	3.98

The effects of pH and concentration of tetrapotassium pyrophosphate on the elution of manganese(III) pyrophosphate are shown in Fig. 1 and 2. The elution is fast, with sharper resolved peak with 1 M tetrapotassium pyrophosphate at pH 6. The elution curve is nearly symmetrical and requires only 50 ml of eluent.

The results of separation of manganese(III) from manganese(II), cobalt(II), nickel(II), copper(II) and selenium(IV) are given in Table 4. Iron(III) forms anionic complex which is taken up by the resin and tellurium(IV) gives a precipitate with pyrophosphate and thus both cannot be separated from manganese(III) by this method.

This ion exchange method can successfully be adopted for the purification of manganese(III) pyrophosphate which can be used as an amperometric titrant for the determination of organic and inorganic complex materials.

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Studies on the Chelation of 3-Hydroxynaphthalene-2-Carboxylic Acid with Zinc(II), Cadmium(II) and Uranyl(II)

S. S. SANDHU, J. N. KUMARIA and R. S. SANDHU*

Department of Chemistry, Guru Nanak Dev University, Amritsar

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The stability constants of the complexes of 3-hydroxynaphthalene-2-carboxylic acid with Zn(II), Cd(II) and UO_2(II) have been obtained potentiometrically in 50 vol % dioxane-water medium at three temperatures and ionic strength 0.1*M* (KNO_3) following the Bjerrum-Calvin technique as applied by Irving and Rossotti. The values of overall changes in $\triangle G$, $\triangle H$ and $\triangle S$ have been evaluated.

The thermodynamic stability constants have also been reported by determining the stability constants of the complexes at 30° and four different ionic strengths and then extrapolating to zero ionic strength.

THE capacity of 3-hydroxynaphthalene-2-carboxylic acid to act as an efficient complexing agent for different metal ions has been studied by various workers under different experimental conditions.[1,2] The stability constants, thermodynamic functions and thermodynamic stability constants of Y(III), Ce(III), La(III), Pr(III), Nd(III), Gd(III), Dy(III), Er(III), Yb(III), Cu(II), Ni(II) and Co(II) complexes with the above ligand in aqueous dioxane (50%, v/v) at three temperatures and four different ionic strengths have already been reported in our earlier communications[3].

In the present study, the stability constants, thermodynamic functions of Zn(II), Cd(II) and UO_2(II) complexes with 3-hydroxynaphthalene-2-carboxylic acid have been determined in aqueous dioxane (50%, v/v) at 20°, 30° and 40° at 0.1*M* (KNO_3) ionic strength following Irving-Rossotti titration technique[4]. Thermodynamic stability constants have also been reported by determining the stability constants of the complexes at 30° and four ionic strengths of 0.05*M*, 0.10*M*, 0.15*M* 0.20*M* (KNO_3) and then extrapolating to zero ionic strength. Attempts to study complexation with Hg(II) resulted in failure because of its precipitation at a very low *p*H.

Experimental

All chemicals used were of AnalaR grade. The double distilled CO_2 free water was used in all experimental work. Dioxane was purified by the recommended procedure[5]. Metal nitrate solutions were prepared by dissolving the corresponding metal salts in double distilled water and standardized by standard volumetric methods. The ligand solution (0.05*M*) was prepared by dissolving in dioxane. The mole ratio of metal to ligand was kept 1 : 5 in order to fulfil the maximum coordination number of the metal ion.

Photovolt digital *p*H meter type M-120 (U.S.A.) caliberated by suitable buffers before use and having an accuracy of ±0.002 units was used to follow the change in *p*H during the titrations which were carried out in a cell immersed in a thermostated bath maintained at 20°±0.1°, 30°±0.1° and 40°±0.1°. The design of the cell was such that it could accommodate a glass stirrer, a micro burette and a glass electrode.

The three solutions (total volume 50 ml in each case) were prepared as follows :

A, $1.0 \times 10^{-2}M$ HNO_3 ; B, $1.0 \times 10^{-2}M$ HNO_3 + $5.0 \times 10^{-2}M$ ligand ; C, $1.0 \times 10^{-2}M$ HNO_3 + $5.0 \times 10^{-2}M$ ligand + $1.0 \times 10^{-2}M$ metal ion solution, such that the concentrations of the common ingredients were identical in different cases. An appropriate quantity of potassium nitrate solution (1.0*M*) was added to maintain the desired ionic strength. The above solutions were titrated against standard potassium hydroxide solution prepared in aqueous dioxane (50%, v/v).

The concentrations were corrected for the changes in volume produced by the addition of alkali during titrations. The difference in the amount of potassium hydroxide utilised for the last two titrations (B and C) is a measure of extent of complexation. From the titration curves it is observed that the metal ligand curve is well separated from the ligand titration curve proving that the liberation of protons is due to chelation.

Results and Discussion

Values of formation functions $\bar{n}_A$, $\bar{n}$ and pL were calculated using the standard expressions[4].

The calculations of practical stability constants of proton complexes were done by plotting $\bar{n}_A$ versus *p*H and then applying various computational methods[6,7]. The mean values of protonation constants of the

TABLE 1—VALUES OF PROTONATION CONSTANTS, STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS AT THREE TEMPERATURES.

Cation	Constants	Method	Temperature 20°	30°	40°	$-\Delta G$ (Kcalmole^{-1}) 20°	30°	40°	ΔH (Kcal mole^{-1}) at 30°	ΔS (cal mole^{-1} degree^{-1}) at 30°
H(I)	$\log {}^{P}K_1^H$		11.52	11.25	10.95					
	$\log {}^{P}K_2^H$		2.78	2.65	2.45					
	$\log {}^{P}\beta_2^H$		14.30	13.90	13.40					
Zn(II)	$\log K_1$	(i)	8.69	8.55	8.35					
		(ii)	8.69	8.55	8.35					
		(iii)	8.55	8.47	8.31					
		(iv)	8.28	8.26	7.98					
	$\log K_2$	(i)	8.42	8 05	8.00					
		(ii)	8.42	—	8.00					
		(iii)	8.43	—	7.97					
		(iv)	8.84	8.34	8.37					
	$\log \beta_2$		17.12	16.60	16.35	22.96	23.01	23.41	−16.2	+22.4
Cd(II)	$\log K_1$	(i)	7.92	7 60	7.43					
		(ii)	7.92	7.60	7.43					
		(iii)	7.92	7.56	7.33					
		(iv)	7.50	7.21	7.04					
	$\log K_2$	(i)	7.65	7.28	7.11					
		(ii)	7.65	7.28	7.11					
		(iii)	7.64	7.22	7.13					
		(iv)	8.07	7.67	7.50					
	$\log \beta_2$		15.57	14.88	14.54	20.88	20.62	20.82	−21.4	− 2.6
UO_2(II)	$\log K_1$	(i)	11.04	10.04	10.06					
		(ii)	—	—	—					
		(iii)	—	—	—					
		(iv)	10.97	9.88	10.01					
	$\log K_2$	(i)	9.78	9.20	8.70					
		(ii)	9.78	9.20	8.70					
		(iii)	9.77	9.20	8.60					
		(iv)	9.85	9.36	8.75					
	$\log \beta_2$		20.82	19.24	18.76	27.92	26.67	26.86	−42.8	−53.4

(i) Bjerrum's half integral method ; (ii) Graphical method ;
(iii) Interpolation at various $\bar{n}$ values ; (iv) Method of successive approximations.

TABLE 2—VALUES OF THE PROTONATION CONSTANTS OF THE LIGAND AND CONCENTRATION STABILITY CONSTANTS OF COMPLEXES AT 30°

Cation	Constants	Method	$\mu = 0.05M$	$\mu = 0.10M$	$\mu = 0.15M$	$\mu = 0.20M$
H(I)	$\log {}^{P}K_1^H$		11.30	11.25	11.20	11.15
	$\log {}^{P}K_2^H$		2.70	2.65	2.60	2.55
	$\log {}^{P}\beta_2^H$		14.00	13.90	13.80	13.70
Zn(II)	$\log K_1$	(i)	8.75	8.55	8.46	8.25
		(ii)	8.75	8.55	8.46	8.25
		(iii)	8.81	8.47	8.44	8.24
		(iv)	8.42	8.26	8.11	8.01
	$\log K_2$	(i)	8.35	8.05	8.08	7.63
		(ii)	—	—	8 08	—
		(iii)	—	—	8.07	—
		(iv)	8.69	8.34	8.43	7.87
	$\log \beta_2$		17.11	16.60	16.54	15.88
Cd(II)	$\log K_1$	(i)	7.98	7.60	7.55	7.25
		(ii)	7.98	7.60	7.55	7.25
		(iii)	7.96	7.56	7.57	7.27
		(iv)	7.68	7.21	7.15	6.98
	$\log K_2$	(i)	7.52	7 28	7.25	6.71
		(ii)	—	7.28	—	—
		(iii)	—	7.22	—	—
		(iv)	7.83	7.67	7.65	6.98
	$\log \beta_2$		15.51	14.88	14.80	13.96
UO_2(II)	$\log K_1$	(i)	10.12	10.04	10.00	9.90
		(ii)	—	—	—	—
		(iii)	—	—	—	—
		(iv)	9.96	9.88	9.92	9.80
	$\log K_2$	(i)	9.30	9.20	8.80	8 86
		(ii)	9.30	9.20	8.80	8.86
		(iii)	9.33	9.20	8.72	8.82
		(iv)	9.46	9 36	8.88	8.97
	$\log \beta_2$		19.42	19.24	18.80	18.77

(i) Bjerrum's half integral method ; (ii) Graphical method ;
(iii) Interpolation at various $\bar{n}$ values ; (iv) Method of successive approximations.

ligand at three temperatures, one ionic strength and four ionic strengths, one temperature have been summarized in Table 1 and Table 2 respectively.

The metal-ligand stability constants have been obtained by analysis of the formation curves obtained by plotting $\bar{n}$ versus pL. These plots indicate that the values of $\bar{n}$ obtained are of the order of two for all the metal ions under study, indicating the formation of both 1 : 1 and 1 : 2 complexes. Bjerrum's half integral method[6], interpolation at various $\bar{n}$ values, graphical method[7] and extended to dioxane-water mixture by Van Uitert and Haas[8] were used to calculate log K_1 and log K_2. In certain cases where there were very few values of $\bar{n}$ below or above one, the value of log K_1 or log K_2 was obtained by interpolation at mid point using the following relationship

$$\log K_1K_2 = 2\,pL \text{ (at } \bar{n} = 1)$$

Both the method of interpolation at various $\bar{n}$ values and graphical method were inapplicable in these cases. Since the ratio of successive constants was less than 10^4, the method of successive approximations[7] was used to refine the values of stability constants obtained by Bjerrum's half integral method. The values of stepwise stability constants obtained by various methods and of overall stability constants obtained by the method of successive approximations have been reported. The error limits are ± 0.05 for log K values.

The small difference between successive constants suggests that the formation of two types of complexes ML_1 and ML_2 proceed simultaneously and may be attributed to the smaller steric hindrance offered by 3-hydroxynaphthalene-2-carboxylic acid as compared with coordinated water molecule.

The data show a decrease in the values of overall protonation constants and stability constants with increase of temperature. The values of overall changes in free energy ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) accompanying complexation have been determined using the temperature coefficient and Gibbs Helmholtz equation[9], using the refined values of stability constants (Table 1). The precision of $\triangle G$, $\triangle H$ and $\triangle S$ values are $\pm$ 0.08 Kcal mole^{-1}, $\pm$ 0.1Kcal mole^{-1} and ± 0.3 cal degree^{-1} mole^{-1} respectively.

$\triangle G$ values for Zn^{2+} complex are more negative with increase of temperature showing that complex formation is a spontaneous process. Whereas for Cd^{2+}, UO_2^{2+} complexes no such regular order is observed. The enthalpy change ($\triangle H$) being negative in all cases is favourable for the formation of these complexes. The entropy change ($\triangle S$) being positive in case of Zn^{2+} complex is favourable but for Cd^{2+} and UO_2^{2+} complexes, $\triangle S^\circ$ being negative does not favour the formation of these complexes.

The metal-ligand stability data at various μ values (Table 2) reveal that log β_2 values decrease with an increase in the ionic strength of the medium. According to Hückel[10], the activity of the metal ion for its interaction with other molecular species varies in inverse proportion to ionic strength of the medium. On this basis, the decrease in stability for 3-hydroxynaphthalene-2-carboxylic acid complexes with the metal ions under study in solution of increasing ionic strength is justified.

The values of log step stability constants at various ionic strengths, extrapolated to zero ionic strength gave step thermodynamic stability constant[11]. These values are shown in Table 3 as log $K_1^{\mu=0}$ and log $K_2^{\mu=0}$. Their sum is shown as calculated log $K^{\mu=0}$. The values of overall stability constants log β_2 at various ionic strengths were likewise extrapolated to zero ionic strength and the overall thermodynamic stability constants thus obtained have been symbolised as experimental log $K^{\mu=0}$

TABLE 3—VALUES OF THERMODYNAMIC STABILITY CONSTANTS AND FREE ENERGIES AT 30°.

	Metal ions		
	Zn(II)	Cd(II)	UO_2(II)
log $K_1^{\mu=0}$	8 56	7.91	10.01
log $K_2^{\mu=0}$	8.96	8.11	9.62
Calcd log $K^{\mu=0}$	17.52	16.02	19.63
Exptl log $K^{\mu=0}$	17.52	16.02	19.63
$\triangle F_1$(Kcal mole^{-1})	−11.86	−10.96	−13.87
$\triangle F_2$(Kcal mole^{-1})	−12.42	−11.24	−13.33
Calcd $\triangle F$(Kcal mole^{-1})	−24.28	−22.20	−27.20
Exptl $\triangle F^\circ$(Kcal mole^{-1})	−24.28	−22.20	−27.20

Ligational standard free energy change was obtained from the expression

$$\triangle F = -2.303RT \log K^{\mu=0}$$

The precision of $\triangle F$ value is $\pm$ 0.08 Kcal mole^{-1}.

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Estimation of Stability Constants of Some Schiff's base Complexes with Lewis acid. A possible role of Intramolecular hydrogen bonding in these Compounds

SOBHI K. AL-DILAIMI and ADEL S. AZZOUZ

Department of Chemistry, University of Mosul, Mosul-Iraq.

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The composition and stability of the Aluminium complexes of some substituted salicylidene aniline Schiff bases were spectrophotometrically determined. The results indicate that these complexes were of 1 : 1 composition and their stability depends on the nature of substituent groups. Intramolecular hydrogen bonding was found to play an important role in the relative stabilities of these complexes.

SCHIFF base complex formation has been of great interest in recent years. Mix[1] has reported the formation of Schiff base complexes as intermediates in some biochemical reactions. Nako[2] has studied the stability of fused rings in metal chelate complexes of Schiff bases prepared by the reactions of salicylaldehyde and dipeptides containing glycine or β-alanine. Harris and coworkers[3] have studied the complex formation of Cu(II), Ni(II), Fe(II) and Mn(II) with tetradentate salicylaldimine Schiff bases.

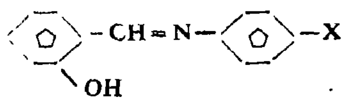
In visual pigments, retinal is attached to a primary amino group associated with the visual protein (opsin). The absorption maxima of these pigments are much higher than the corresponding aldehydes. These observations aroused our curiosity to study the environmental factors that can change the absorption properties of these Schiff bases. Most of the previous work has been concerned with transition metal-Schiff base complexes. The present work was undertaken to study the various factors affecting the stability constants of complexes formed by the reaction of $AlCl_3$ and salicylidene aniline Schiff bases containing different substituents. Al^{+3} has been chosen as a representative non transition element which is known to catalyze a variety of reactions involving Schiff bases, probably through the formation of intermediate Al-Schiff base complexes. In addition $AlCl_3$ has a much better solubility in ethanol than other salt.

Experimental

Salicylidene-aniline, salicylidene-*p*-methoxyaniline, salicylidene-*p*-methylaniline, and salicylidene-*p*-bromoaniline were prepared according to the procedure described by El-Bayoumi and coworkers[4]. The molecular structure of these compounds has been established by spectroscopic methods, as illustrated in Table 1.

Aniline, *p*-toluidine, *p*-anisidine and ethanol were purified by standard methods.

TABLE 1—SPECTRAL PROPERTIES OF THE LIGANDS



Substituent (X)	M.P. (°C)	U. V. spectra in ethanol (nm.)	I. R. spectra in $CHCl_3$ (cm.$^{-1}$)
H	48-50	230, 270, 238	1625
CH_3O	88-89	234, 268, 350	1627, 1601, 1485
CH_3	81-82	233, 271, 342	1624, 1110
Br	100	234, 271, 342	1620, 1600

p-Bromoaniline (BDH) was used without further purification. The ultra violet absorption spectra were recorded by Unicam SP 800 and SP 500 spectrophotometers; using 1 cm quartz cells.

Results and Discussion

In the following discussion, salicylidene-*p*-methoxyaniline complex has been chosen as a representative of the series.

The wavelength of maximum absorption of the $AlCl_3$ complexes of this Schiff base was centered at 396 nm. The absorbances of a series of solution containing a fixed amount of $AlCl_3$ solution and variable excess of Schiff base were measured at the above mentioned wavelength. The maximum absorbance was obtained by mixing 1.5 ml of 5×10^{-4} M Schiff base with 0.25 ml of $AlCl_3$, $5\times10^{-4}M$. i.e., when the metal : ligand molar ratio is 1 : 6 (Table 2)

TABLE 2—EFFECT OF METAL : LIGAND MOLAR RATIO ON ABSORBANCE USING SCHIFF BASE (II)*

ml. of 5×10^{-4} *M* $AlCl_3$	ml. of 5×10^{-4} *M* Schiff base	Absorbance
0.25	0.25	0.050
0.25	0.50	0.067
0.25	0.75	0.100
0.25	1.00	0.115
0.25	1.50	0.180
0.25	2.00	0.180
0.25	2.25	0.175

* Formula are given in Table 3.

dissociated. The degree of dissociation α can then be determined from the equation :

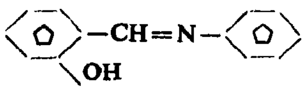
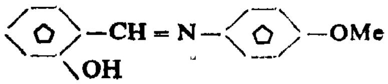
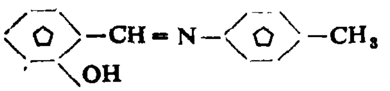
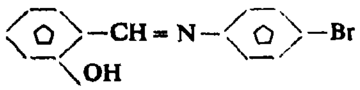
$$\alpha = (A_m - A_s)/A_m$$

If the original concentration of the complex is C, the stability constant for a 1 : 1 complex is then given by :

$$K = 1 - \alpha/\alpha^2 C$$

The concentration C is assumed to be equal to that of metal ion, since the latter reacts completely with the ligand. The average values of the apparent stability constant K and the stability periods are given in Table 3.

TABLE 3—CALCULATED PARAMETERS FOR SALICYLIDENE ANILINE-$AlCl_3$ COMPLEXES

Ligand		λ_{max} for complex (nm)	Metal/ligand molar ratio for max. absorbance	Stability period (min)	Apparent stability constant K*
	(I)	396	1 : 4	1.5	0.386×10^4
	(II)	396	1 : 6	3.0	2.150×10^4
	(III)	390	1 : 6	3.0	1.410×10^4
	(IV)	401	1 : 6	1.0	0.271×10^4

K* = Average of three readings.

The stability period of this complex was obtained by measuring the absorbance of the solution of maximum absorbance as a function of time at 396 nm. The time interval during which the colour was stable was found to be three minutes.

The composition of these complexes has been determined by three different methods, namely the continuous variation method by Job[5], the mole ratio method[6] and the slope ratio method[7]. The result indicated that all the complexes were of 1 : 1 type.

The apparent stability constants were determined by the method of Harvey and Manning[7]. This method involves the measurement of the absorbance, A_s of a solution containing stoichiometric amounts of metal and ligand, and is considered to be highly dissociated. The absorbance A_m of another solution containing the metal and a large excess of the ligand is also determined. This solution is assumed to be only very slightly

It is observed from these results that the stability constants of this series are a function of the substituent present on the aniline ring. The value is decreasing in the order of :

$$p\text{—}OCH_3 > p\text{—}CH_3 > p\text{—}H > p\text{—}Br$$

This variation could be due to the decreasing inductive effect of the substituent. The more the electron donating power of the group is, the higher would be the electron density around the nitrogen, which results in greater stability. These results clearly indicate the dependence of the stability constants of these complexes on the electron density on the nitrogen atom.

The stability constants of benzylidene aniline series with the same substituents were examined previously[8]. The values of these constants for this series were found to be much higher than the values obtained for the salicylidene series. Present studies showed the effect of

the *o*-hydroxyl group in decreasing the value of stability constant. This effect at the first glance was unexpected since the hydroxyl group is an electron donating group.

Charette and his coworkers[9], observed that a Schiff base of N-salicylidene-2 aminopropane exists chiefly in the form of intramolecular hydrogen bonding as shown in Fig. 1.

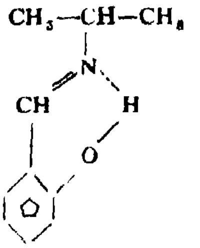


Fig. 1

Such a hydrogen bonded six membered ring may also exist in salicylidene aniline series. This hydrogen bond formation may result in decreased electron density around nitrogen, thus giving rise to a lower value of stability constants. Model building of such a compound support H-bonding without any increase in the steric hindrance in the molecule. However, the possibility of decreased stability by steric hindrance is not excluded.

Salicylidene-*p*-bromoaniline has a stability constant value of 0.271×10^4, while the value of benzylidene-*p*-bromoaniline could not be obtained experimentally, because of the possible fast dissociation of the complex. The possible reason for these results could be the competition between the ortho hydroxyl group for hydrogen bond formation with the unpaired electrons of nitrogen, and the electron withdrawing ability of bromine, thus making the electron density around the nitrogen less available for bromine. This could also result in a decreased conjugation of the unpaired electrons of nitrogen with the pi-electrons of the phenyl ring. On the other hand, in benzylidene-*p*-bromoaniline, the electrons around the nitrogen are in full conjugation with the phenyl ring, and consequently to theelectron withdrawing effect of the bromine resulting in an unmeasurable stability constant value.

Conclusion

The stability constant values of the salicylidene aniline complexes with $AlCl_3$ were found to depend upon electron density around the nitrogen atom. The increased electron density is due to the increased electron donating power of the substituents. *o*-Hydroxyl group was found to play an important role in hydrogen bond formation, resulting in a decrease electron density around the nitrogen and less conjugation of the unpaired electron with the phenyl ring, causing a lower value in the stability constants.

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Study of Some Mixed Complexes of Yttrium(III)

A. M. PUJARI & K. N. MUNSHI

Department of Chemistry, Nagpur University. Nagpur, India

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The tendency of 1 : 1 Y(III)-Ethylenediaminetetraacetic acid (EDTA) and N-Hydroxyethylethylenediaminetriacetic acid (HEDTA) chelates to form mixed ligand, 1 : 1 : 1 chelates with 8-hydroxyquinoline 5-sulphonic acid (OSA), 8-hydroxy-7 iodoquinoline 5-sulphonic acid (IOSA). Pyrogallol (PGL), Protocatechuic acid (PCA) and 3.5 dinitrosalicylic acid (DNSA) has been investigated by potentiometric method at three different temperatures and at fixed ionic strength $\mu = 0.2$.

THE tendency of lanthanides to expand their coordination number, greater than six has been reported by different workers, in the study of the mixed ligand complexes[1-4].

The present communication describes the results obtained on the study of some mixed ligand complexes of yttrium using ethylendiamine-tetraacetic acid (EDTA) and N-hydroxyethylethylenediaminetriacetic acid (HEDTA) as primary ligands (A) and 8-hydroxyquinoline 5-sulphonic acid (OSA), 8-hydroxy-7-iodoquinoline 5-sulphonic acid (IOSA), pyrogallol (PGL), protocatechuic acid (PCA) and 3.5 dinitrosalicylic acid (DNSA) as secondary ligand (L). All these ternary systems are being reported here, for the first time. The secondary ligands are chosen in such a manner that exchange does not occur between primary and secondary ligand, i.e., the primary complexes are very stable[5,6] in comparison to the complexes formed between yttrium(III) and secondary ligand. Modified method of Irving and Rossotti technique have been used[7].

Experimental

Material :

All chemicals employed were of reagent grade purity. The ligand solutions were prepared using disodium salt of EDTA (BDH), HEDTA (Sigma), DNSA (E. Merck), OSA (E. Merck), IOSA (BDH) and protocatechuic acid (BDH). Pyrogallol was purified and its solution was prepared in oxygen free double distilled water to avoid its oxidation. This solution was always freshly prepared. All ligand solutions were standardised potentiometrically. Metal solution was prepared from $Y(NO_3)_3 \cdot 6H_2O$ (BDH) in known quantity of nitric acid, to prevent the hydrolysis and was estimated by complexometric titration[8].

Procedure :

The experimental procedure involved potentiometric titration against Sodium hydroxide (1.152*M*) of four mixtures as described in our earlier papers[3,4]. The ionic strength of solution was adjusted to 0.2*M* using an appropriate amount of neutral potassium nitrate

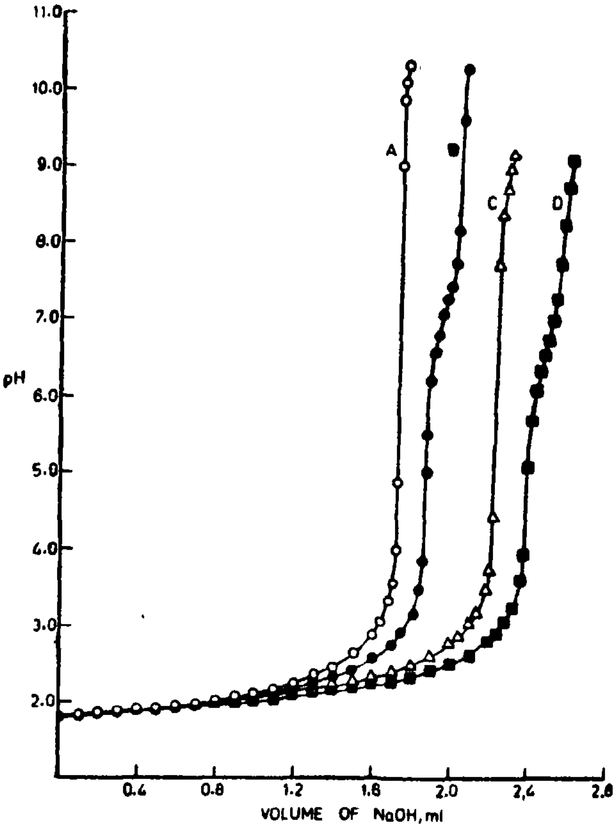


Fig. 1. Titration curve for the yttrium-HEDTA-DNSA mixed ligand complex at 25° at $\mu = 0.2M$.

Curve A : $1.998 \times 10^{-2} M$ Nitric acid.

Curve B : $1.998 \times 10^{-2} M$ Nitric acid, $2 \times 10^{-3} M$ DNSA

Curve C : $1.998 \times 10^{-2} M$ Nitric acid, $2 \times 10^{-3} M$ HEDTA, $2 \times 10^{-3} M$ Y(III)

Curve D : $1.998 \times 10^{-2} M$ Nitric acid, $2 \times 10^{-3} M$ HEDTA, $2 \times 10^{-3} M$ DNSA, $2 \times 10^{-3} M$ Y(III).

solution. Final volume of all the systems was adjusted to 100 ml by using double distilled water. Titrations were carried out in nitrogen atmosphere at three different temperatures[3,4].

The ratio of Y(III) : Primary ligand : Secondary ligand was always kept 1 : 1 : 1 in each system. Typical plots of *p*H against volume of alkali have been shown in Fig. 1 and 2 for Y(III)-EDTA-DNSA systems and

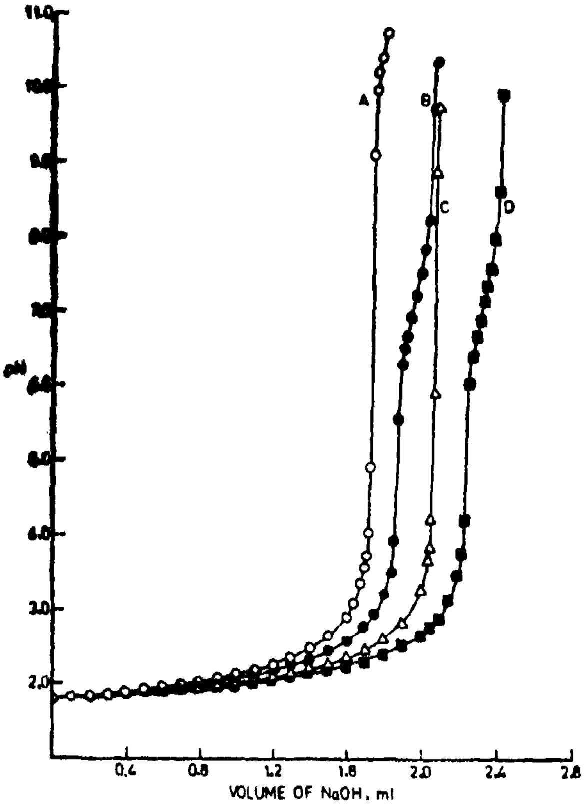


Fig. 2. Titration curve for the yttrium-EDTA-DNSA mixed ligand complex at 25° at $\mu = 0.2M$.

Curve A : $1.998 \times 10^{-3} M$ Nitric Acid.

Curve B : $1.998 \times 10^{-3} M$ Nitric Acid, $2 \times 10^{-3} M$ DNSA.

Curve C : $1.998 \times 10^{-3} M$ Nitric Acid, $2 \times 10^{-3} M$ EDTA, $2 \times 10^{-3} M$ Y(III).

Curve D : $1.998 \times 10^{-3} M$ Nitric Acid, $2 \times 10^{-3} M$ EDTA, $2 \times 10^{-3} M$ DNSA, $2 \times 10^{-3} M$ Y(III).

Y(III)-HEDTA-DNSA. Similar plots were obtained for other systems also. Titration with 1 : 1 : 2 (Y: A: L) have also been performed. It was found in all cases that the nature of curves tally exactly to 1 : 1 : 1 titration, indicating that further expansion of coordination number of Y(III) is not possible.

Results and Discussions

The values of protonation constants as calculated by the method of interpolation at various $\bar{n}_A$ values are given in Table-1 and have been taken into account for the calculation of the formation constant of ternary systems.

TABLE 1—STEPWISE PROTONATION CONSTANT OF THE SECONDARY LIGAND AT VARIOUS TEMPERATURES. ($\mu = 0.2$ *M*)

Ligand	Constants	25°	35°	45°
OSA	$\log K_1^H$	8.34	8.20	8.08
	$\log K_2^H$	3.92	3.82	3.73
IOSA	$\log K_1^H$	6.97	6.74	6.66
	$\log K_2^H$	2.46	2.38	2.28
DNSA	$\log K_1^H$	7.52	7.26	7.21
PGL	$\log K_1^H$	10.98	10.82	10.68
	$\log K_2^H$	8.90	8.71	8.57
PCA	$\log K_1^H$	8.97	8.94	8.84
	$\log K_2^H$	4.51	4.49	4.45

From the titration curves, (Fig. 1 and 2) it is observed that primary complex formation (curve C), takes place at very low *p*H, and the calculations show that it is stable upto *p*H~10 in both the cases (using EDTA and HEDTA as primary ligands). Primary complex curve C and mixed complex curve D overlap each other at lower *p*H, indicating that in this range, where primary ligand combines with Y(III), attachment of secondary ligands does not take place. The mixed complex curve D, separates from primary complex curve C at *p*H 2.0 due to self dissociation of the secondary ligand (DNSA). After *p*H 4, mixed complex curve shows the indication of attachment of secondary ligand with yttrium. Since, the dissociation of Y-A does not take place in the range of dissociation of secondary ligand, it can be considered that secondary ligand combines the Y(III)-A. In presence of secondary ligand, formation of $Y(III)\text{-}A(OH)_n$ is also suppressed.

The $\bar{n}$ values were calculated taking into consideration the difference from curves C and D from which the difference of curve A and B is subtracted at various *p*H values[3,4]. A typical plot of $\bar{n}$ against pL for Y(III)-HEDTA-DNSA and Y(III)-EDTA-DNSA systems have been shown in Figs. 3 and 4. Other systems also have similar plots. The value of $\log K^{MA}_{MAL}$ have been evaluated using the method of interpolation at various $\bar{n}$ values and are summarised in Table-2. The error limits are of $\pm$ 0.06 log units.

An observation of the results reported earlier[3,4] and also in the present paper on the mixed ligand complexes of yttrium, with different primary ligands (keeping secondary bidentate ligand same), shows that the trend in the stability constant is based on the number of vacant coordination position of yttrium,

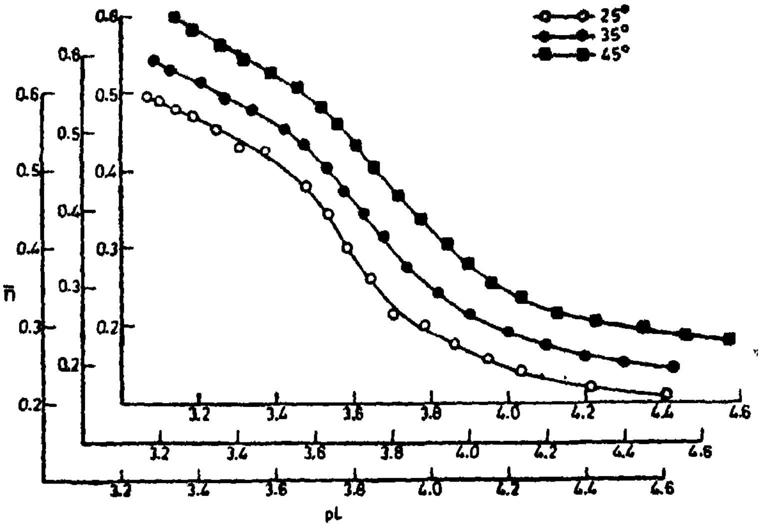


Fig. 3. Formation curve of [Y(III)(HEDTA)(DNSA)] at different temperatures.

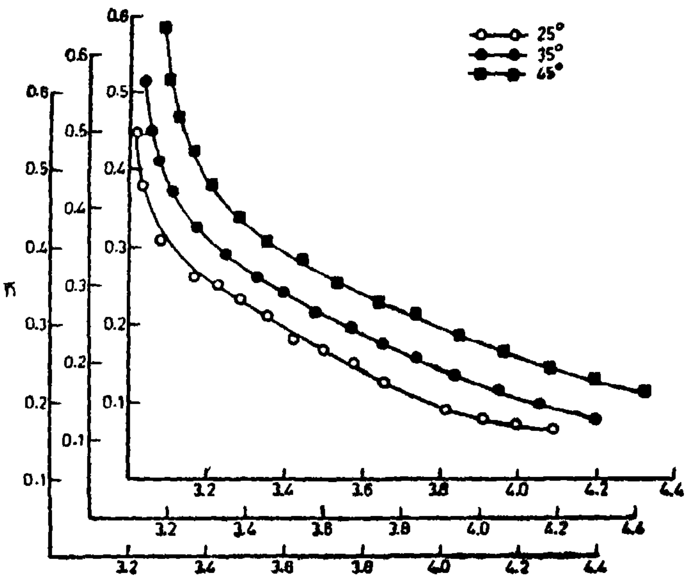


Fig. 4. Formation curve of [Y(III)(EDTA)(DNSA)] at different temperatures.

TABLE 2—STABILITY CONSTANTS OF MIXED LIGAND COMPLEXES OF Y(III) AT VARIOUS TEMPERATURES ($\mu = 0.2$ M)

System	Constants	t = 25°	t = 35°	t = 45°
Y(III)-HEDTA-OSA	log K_1	4.90	4.82	4.75
Y(III)-EDTA-OSA	log K_1	3.95	3.88	3.82
Y(III)-HEDTA-IOSA	log K_1	4.68	4.57	4.48
Y(III)-EDTA-IOSA	log K_1	3.80	3.74	3.60
Y(III)-HEDTA-PGL	log K_1	5.77	5.44	5.27
Y(III)-EDTA-PGL	log K_1	5.16	5.09	4.81
Y(III)-HEDTA-PCA	log K_1	3.87	3.80	3.77
Y(III)-EDTA-PCA	log K_1	3.45	3.38	3.34
Y(III)-HEDTA-DNSA	log K_1	3.62	3.53	3.47
Y(III)-EDTA-DNSA	log K_1	3.25	3.20	3.17

capacity of yttrium to expand its coordination number from six to seven or eight and also on the nature of the primary complex species formed.

Thus, depending on the number of vacant coordination positions, it is found that the mixed complexes with NTA (tetradentate) is more stable than HEDTA (pentadentate) which in turn is more stable than EDTA (hexadentate). When NTA is used as primary ligand, the expansion of coordination number is not required. In case of HEDTA, and EDTA, however, coordination number has to be increased to seven or eight respectively

to account for these mixed ligand complex formation. The expansion of coordination number suggests the formation of less stable complexes is evident from the present study.

[Y(NTA)] and [Y(HEDTA)] primary complex species are neutral in nature and thus, do not repel the incoming negatively charged secondary ligand. EDTA, however, forms a [Y(EDTA)] negatively charged species causing an electrostatic force of repusion for the incoming negatively charged secondary ligands giving lower stability of mixed ligand complexes of yttrium-EDTA.

The mixed ligand complex of OSA is more stable than that of IOSA as it contains an electron withdrawing iodo group. So the basicity of reagent decreases and it forms less stable complex than OSA. Similary, in case of PGL, PCA and DNSA the order of stability of mixed complexes decrease as PGL > PCA > DNSA.

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Potentiometric Studies on the Systems Zn(II)/Cd(II)-Nitrilotriacetic acid-Dicarboxylic acids.

KIRAN KAPOOR, VINOD KUMARI, R. C. SHARMA and G. K. CHATURVEDI

Chemical Laboratories, Agra College, Agra

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Formation of 1 : 1 : 1 ternary complexes in the system : Zn(II)/Cd(II)-NTA-H_2A (where H_2A = oxalic (OX), malonic (MALN), succinic (SUC), phthalic acid (PHA)) has been evidenced potentiometrically. The formation constants and thermodynamic functions viz. $\triangle G$, $\triangle H$ and $\triangle S$ have been calculated for the resulting complexes at 25±1° and 35±1°. The order of stability in terms of metal is Zn(II) > Cd(II).

A survey of the literature revealed that the formation of mixed ligand complexes M(II)-X-Y (where M(II) = Zn(II), Cd(II) ; X = diamines, heterocyclic bases and Y = mono or dicarboxylic acids and their substituted derivatives) have been reported[1-5]. Tandon and coworkers[6] have carried out potentiometric studies on the ternary systems Zn(II)-NTA-hydroxy acids. However, no work appears to have been done on the systems Zn(II)/Cd(II)-NTA-dicarboxylic acids. Therefore, it has been considered worthwhile to undertake potentiometric studies on some of these systems with a view to determine the formation constants and the thermodynamic functions i.e. free energies of formation ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) changes for the resulting species.

Materials : All the chemicals used were of Analar BDH grade. Stock solutions of zinc nitrate and cadmium nitrate were prepared by dissolving zinc oxide and cadmium carbonate in nitric acid. The solutions were standardised gravimetrically for Zn(II) and Cd(II) as zinc ammonium phosphate and cadmium anthranilate respectively.

Standard solution of dicarboxylic acids H_2A : oxalic acid (OX), malonic (MALN), succinic (SUC) and phthalic acid (PHA) were prepared by direct weighing. NTA was used as its disodium salt. The concentrations of all the ligands were checked by *p*H titrations.

Instruments : The *p*H measurements were recorded with a Precision Philips *p*H meter (PR 9405 *M*) at 25 ± 1° and 35±1° (maintained in a thermostat). The instrument was standardised with 0.05 *M* potassium hydrogen phthalate (*p*H = 4). Ionic strength ($\mu = 0.1 M$ KNO_3), total volume (50 ml) and the concentration (5×10^{-3} *M* in terms of metal and the ligands) were kept constant at the beginning of the titration.

Calculations : The pK values of oxalic, malonic, phthalic acids and NTA were calculated by the method of Chaberek and Martell[7] and that of succinic acid by the Noyes method[8]. The calculated values determined at 25±1° and 35±1° for dicarboxylic acids H_2A, (OX – pK_1 = 1.65, pK_2 = 4.14 ; MALN—pK_1 = 2.95, pK_2 = 5.82 ; SUC—pK_1 = 4.19, pK_2 = 5.49 ; PHA—pK_1 = 3.39, pK_2 = 5.46) are in accordance with Sergeant[9] whereas pK_1 of NTA at the respective temperatures are found to be 9.82 and 10.05.

Formation constants ($K_{MLL'}$) of the ternary complexes formed by the simultaneous addition of the two ligands were calculated by the method of Ramamoorthy and Santappa[10].

The free energies of formation ($\triangle G$), enthalpy ($\triangle H$) and entropy ($\triangle S$) changes at 25±1° and 35±1° were calculated by the following expressions :

$$\triangle G = -RT\ln K_{MLL'}$$

$$\triangle H = \frac{2.303\ RT_1T_2\ (\log \beta_2 - \log \beta_1)}{T_2 - T_1}$$

$$\triangle S = \frac{\triangle H - \triangle G}{T}$$

where R is the gas constant,

T_1 and T_2 are the temperatures in absolute degrees β_1 and β_2 are the formation constants at T_1 and T_2 respectively,

The values of $\triangle G$. $\triangle H$ and $\triangle S$ are given in table 1.

Results and Discussion

System M(II)-NTA

On titrating the solution containing equimolar ratio of Zn(II) or Cd(II) and NTA, a sharp inflection at m = 1 (where m = moles of base added per mole of ligand) in curve a and a′ for Zn(II) and Cd(II) respectively in

TABLE I

System	$\log K_{MLL'}$		ΔG (Kcal/mole)		ΔH	ΔS(cal/mole/degree)	
	25 ± 1°C	35 ± 1°C	25 + 1°C	35 + 1°C	(Kcal/mole)	25 + 1°C	35 + 1°C
Zn(II)-NTA-OX	7.88 ± 0.16	7.69 ± 0.13	- 10.740	- 10.835	- 7.980	+ 9.261	+ 9.269
Cd(II)-NTA-OX	7.21 ± 0.14	7.02 ± 0.13	- 9.827	- 9.891	- 7.980	+ 6.198	+ 6.204
Zn(II)-NTA-MALN	12.20 ± 0.19	12.02 ± 0.20	- 16.628	- 16.936	- 7.560	+ 30.429	+ 30.441
Cd(II)-NTA-MALN	11.16 ± 0.21	11.04 ± 0.23	- 15.279	- 15.555	- 7.140	+ 27.312	+ 27.321
Zn(II)-NTA-SUC	12.93 ± 0.30	12.75 ± 0.34	- 17.623	- 17.964	- 7.560	+ 33.769	+ 33.779
Cd(II)-NTA-SUC	12.13 ± 0.34	11.90 ± 0.33	- 16.532	- 16.767	- 9.660	+ 23.063	+ 23.074
Zn(II)-NTA-PHA	12.03 ± 0.18	11.86 ± 0.24	- 16.396	- 16.710	- 7.140	+ 31.060	+ 31.071
Cd(II)-NTA-PHA	11.16 ± 0.23	10.97 ± 0.26	- 15.211	- 15.456	- 7.980	+ 24.265	+ 24.272

Fig. I, indicates the formation of 1 : 1 binary M(II)-NTA complex as depicted below :

$$M^{2+} + NTA^{3-} \xrightarrow{m=1} [M^{2+}\ NTA^{3-}]$$

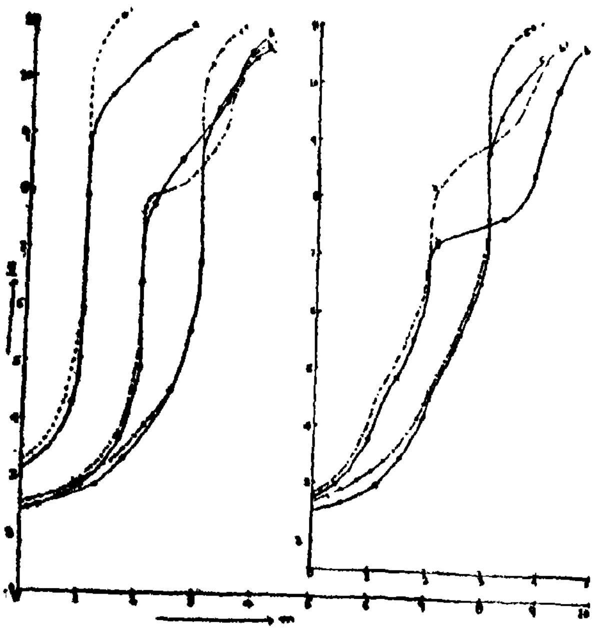
M(II) - H₂A

The curves b and b′ in Figs. I—IV for the binary systems involving Zn(II), Cd(II) respectively, in the presence of equimolar amount of H_2A, exhibit inflections at m = 2 due to the formation of 1 : 1 M(II) - H_2A binary complex. Another inflection at m≈4 may be attributed to the disproportionation of the initially formed binary species giving more stable 1 : 2 complex with the precipitation of a part of the metal as hydrated metal oxide

$$M^{2+} + H_2A \xrightarrow{m=2} [M^{2+}A^{2-}] \xrightarrow{m\approx 4} 1/4\ [M^{2+}(A^{2-})_2] + \tfrac{3}{4}\ MO.H_2O + \tfrac{1}{2}\ A^{2-}$$

System M(II) - NTA - H₂A

Curves c and c′ in Figs. I - IV represent the ternary systems involving 1 : 1 : 1 Zn(II)/Cd(II)←NTA—H_2A. A single sharp inflection at m=3 may be correlated to the formation of 1 : 1 : 1 ternary complex by the simultaneous addition of two ligands to the metal ion. The formation of ternary species is further supported by the non-appearance of a solid phase during the



I   Fig. II

Fig. I curve a = Zn(II)-NTA, a′ = Cd(II)-NTA ; b = Zn(II)-OX, b′ = Cd(II)-OX ; c = Zn(II)-NTA-OX, c′ = Cd(II)-NTA-OX

Fig. II curve b = Zn(II)-MALN, b′ = Cd(II)-MALN; c = Zn(II)-NTA-MALN, c′ = Cd(II)-NTA-MALN.

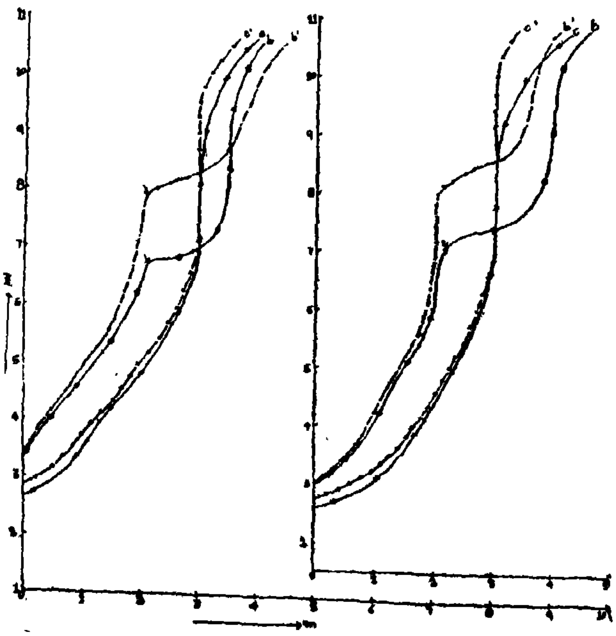


Fig. III   Fig. IV

Fig. III curve b = Zn(II)-SUC, b′ = Cd(II)-SUC ; c = Zn(II)-NTA-SUC, c′ = Cd(II)-NTA-SUC.

Fig. IV curve b = Zn(II)-PHA, b′ = Cd(II)-PHA, ; c = Zn(II)-NTA-PHA, c′ = Cd(II)-NTA-PHA

titration:

$$M^{2+} + NTA^{3-} + H_2A \xrightarrow{m=3} \left[NTA^{3} \cdot M^{2+}A^{2-}\right]$$

(where H_2A=OX, MALN, SUC or PHA).

A comparison of the values of formation constants of the ternary species show the order of stability in terms of metal as Zn(II)>Cd(II) in accordance with the Williams Irving[11] series whereas in terms of dicarboxylic acids the order of stability is OX<MALN≈SUC≈PHA which may be attributed to the increasing basicities : OX<MALN≈SUC≈PHA probably caused by the increasing inductive influence of CH_2 groups in the ligand molecules. Increasing size of the dicarboxylic acid ions (A^{2-}) show a progressive increase to the extent to which polarization of the (A^{2-}) by metal ion is caused. Larger the magnitude of polarization, stronger is the covalent bond formed. The other factor such as presence of as many as three, five-membered rings resulting from the chelation of the metal-ion with NTA may also play an important role and cannot be set-aside while discussing the stabilities of the above ternary species.

The values of $\triangle G$ and $\triangle S$ (table 1) correspond to the formation constants of the respective ternary species. The increasing positive values of $\triangle S$, give more negative values of $\triangle G$. More the negative value of $\triangle G$, stronger is the complex formed.

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Spectrophotometric Study of the Reaction of Osmium with Promethazine Hydrochloride

H. SANKE GOWDA and B. KESHAVAN

Department of Post-graduate Studies and Research in Chemistry, University of Mysore, Manasa Gangotri, Mysore.

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Promethazine hydrochloride is proposed as a new reagent for the spectrophotometric determination of microgram amounts of osmium. It forms a red coloured species with osmium(VIII) or osmium(VI) at room temperature in hydrochloric acid medium. The red species exhibits maximum absorbance at 515 nm. Beer's law is valid over the concentration range, 0.2-4.8 ppm for osmium(VIII) and 0.16-6.0 ppm for osmium(VI). The Sandell's sensitivity of the reaction is 0.021 μg/cm² for osmium(VIII) and 0.015μg/cm² for osmium(VI). The effects of time, temperature, acidity, order of addition of reagents, reagent concentration and diverse ions are reported.

THE authors reported the use of promethazine hydrochloride, PH, 10-(2-dimethylaminopropyl) phenothiazine hydrochloride for the spectrophotometric determination of palladium(II)[1] and ruthenium(III)[2]. The present work describes PH as a sensitive reagent for the rapid spectrophotometric determination of osmium(VIII) and osmium(VI). The proposed method offers the advantages of simplicity, sensitivity, reasonable stability and wider range of determination without the need for heating or extraction.

Experimental

Beckman Model DB Spectrophotometer with 1.0 cm silica cells was used for all absorbance measurements.

Standard Os(VIII) and Os(VI) solutions

A stock solution of osmium(VIII) was prepared from osmium tetroxide (M/s Johnson Matthey Chemicals Ltd., London) in 0.2*M* sodium hydroxide. The solution was standardised iodometrically[3]. Standard solution of osmium(VI) was prepared from potassium osmate (J.M.C.) in doubly distilled water. The stock solutions were further diluted to give standard solutions of 20 μg/ml.

Promethazine hydrochloride solution

A 0.2% aqueous solution of PH (May & Baker) was prepared and stored in a refrigerator. The reagent solution was stable for about one month.

Other reagents

The solutions of acids and diverse ions of suitable concentrations were prepared in double distilled water using analytical grade reagents.

Procedure for the determination of osmium(VIII) or osmium(VI)

An aliquot of the stock solution containing 5 to 120 μg of osmium(VIII) or 4 to 150 μg of osmium(VI) was transferred to a 25 ml volumetric flask. 10 ml of 7.5*M* hydrochloric acid and 4 ml of 0.2% PH solution were added and the solution was diluted to the mark with doubly distilled water. The solution was mixed well and the absorbance was measured at 515 nm after standing 15 minutes against a reagent blank prepared in the same way. The amount of osmium in the sample solution was then deduced from the standard calibration curve.

Results and Discussion

PH forms a red coloured species which is believed to be a radical cation with osmium(VIII) or osmium(VI) in hydrochloric acid medium at room temperature (27° ± 1°). Osmium(IV) does not give any coloured product with PH. The sensitivity of the reaction and stability of the colour in four acids (3N) are in the order of $HCl > H_2SO_4 > H_3PO_4 > HAc$. Although the colour development is initially rapid, a period of 15, 25, 45 and 50 minutes is required to reach the maximum intensity of colour for osmium(VIII) and osmium(VI) in HCl, H_2SO_4, H_3PO_4 and HAc respectively. The absorbance values remain constant for 45, 20, 15 and 10 minutes for osmium(VIII) and 35, 15, 10 and 5 minutes for osmium(VI) in 3*N* HCl, H_2SO_4, H_3PO_4 and HAc respectively. Hence hydrochloric acid medium was chosen for all subsequent studies.

Optimum acid range

Maximum absorbance is achieved in 2.0-4.0*M* hydrochloric acid for both osmium(VIII) and osmium(VI). Below 2.0*M* acid concentration the development of red colour is slow. The reagent is slowly oxidised at acidities higher than 4.0 *M*. Nitric acid or any other medium containing oxidising species cannot be used as it oxidises PH to a red coloured species.

Absorbance curves

The absorption spectra of PH, osmium(VIII) and red species are shown in Fig. 1. The red species exhibits maximum absorbance at 514-518 nm. The absorption spectra of PH and osmium(VIII) or osmium(VI) show that they do not absorb at this wavelength. Subsequent studies were made at 515 nm.

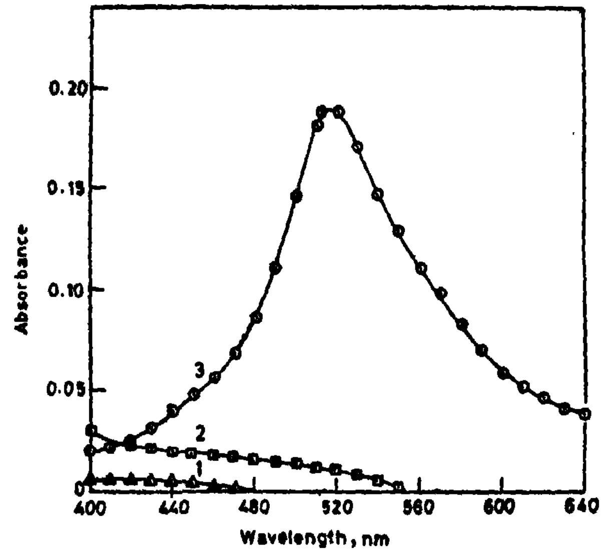


Fig. 1. Absorption spectra of reagent blank, osmium (VIII) and red species. 1. Reagent blank ; 2. Osmium (VIII) and 3. Red species (Os = 4 ppm, HCl = 3N).

Effect of varying reagent concentrations

A 16-fold molar excess of the reagent is required in order to obtain the maximum intensity of colour. The optimum amount of the reagent is 4 ml of 0.2% PH solution in a final volume of 25 ml.

Adherence to Beer's law and optimum range

Beer's law is valid over the concentration range 0.2-4.8 ppm of osmium(VIII) and 0.16-6.0 ppm of osmium(VI). The optimum concentration range for the effective spectrophotometric determination as evaluated by Ringbom's method[4,5] is 1.0-4.4 ppm for osmium(VIII) and 1.0-5.0 ppm for osmium(VI).

Sensitivity and Molar absorptivity

For $\log I_0/I = 0.001$, the sensitivity of the reaction as calculated from Beer's law data is 0.021 $\mu g/cm^2$ for osmium(VIII) and 0.015 $\mu g/cm^2$ for osmium(VI). The respective molar absorptivities are 8.9×10^3 l mol^{-1}cm^{-1} and 1.23×10^4 l mol^{-1}cm^{-1} at 515 nm.

Order of addition of reagents

It is found that there is no appreciable change in the absorbance or in colour intensity of the red species if the order of addition of reagents is varied.

Effect of temperature

The red species formed by osmium(VIII) or osmium(VI) with PH is stable over the temperature range 4-40° as shown by the constant absorbance readings.

Effect of diverse ions

The effect of anions and cations which often accompany osmium(VIII) are studied. The results are summarised in Table 1. Efforts to increase the tolerance limit of cations by the addition of masking agents were unsuccessful.

TABLE—1. TOLERANCE LIMIT OF DIVERSE IONS IN THE DETERMINATION OF 3 PPM OF OSMIUM(VIII)

Ion added	Tolerance limit, ppm	Ion added	Tolerance limit, ppm
F^-	1100	Fe^{3+}	4.0
Cl^-	7850	Co^{2+}	100.0
Br^-	1870	Ni^{2+}	585.0
I^-	5	Cu^{2+}	35.0
NO_3^-	2065	Ru^{3+}	0.5
PO_4^{3-}	1375	Rh^{3+}	12.0
SO_4^{2-}	1000	Pd^{2+}	0.5
CH_3COO^-	5345	Ir^{3+}	11.0
$C_2O_4^{2-}$	950	Pt^{4+}	10.0
EDTA	4720	Au^{3+}	0.5

Sample solutions containing 4μg/ml of osmium(VIII) or osmium(VI) prepared by the standard procedure gave a relative error of $\pm 0.7\%$ and standard deviation of 0.002.

Determination of osmium in alloys

Synthetic mixtures corresponding to osmiridium alloy were prepared and the osmium content was determined following the standard procedure. The results are given in Table 2.

TABLE—2. DETERMINATION OF OSMIUM IN SYNTHETIC MIXTURES CORRESPONDING TO OSMIRIDIUM ALLOY.

Os(VIII) taken, ppm	Ir (III) added, ppm	Os(VIII) found, ppm	Standard deviation, ppm
1.2	0.3	1.196	0.004
2.4	0.6	2.394	0.003
3.6	0.9	3.592	0.002
4.8	1.2	4.790	0.003

*The amount of osmium (VIII) found is based on ten determinations.

The sensitivity of the proposed method is found to be more than that of 2-mercaptobenzimidazole[6], 2-mercaptobenzothiazole[7], 1-carbamidino-3-methyl-5-pyrazolone[8], acenaphthenequinone monoxime[9] and rubeanic acid[10] which have been proposed as sensitive spectrophotometric reagents for osmium(VIII).

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Benzoyl-*m*-Nitro-Acetanilide as A Gravimetric Reagent for Cadmium

PRADIP KUMAR DAN and JYOTIRMOY DAS

Department of Chemistry, The University of Burdwan, Burdwan 713101

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Cadmium (14-23 mg) has been quantitatively precipitated with benzoyl-*m*-nitro-acetanilide and the highly insoluble yellow-coloured bis complex has been dried at 110° for weighing. The conversion factor is 0.1656. The relative standard deviation is ±0.14%. Separation from Ni^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Pb^{2+}, Mg^{2+}, Al^{3+}, In^{3+} and Cr^{3+} was possible using sodium or magnesium-EDTA as the masking agent. Thermogravimetric studies indicated the complex to be stable upto 410°.

VERY few gravimetric methods for cadmium have been reported and due to its softness this metal ion shows preference to ligands such as amines, cyanides and sulphide ions. Thus thiourea-Reinecke's salt[1,2] method has been used widely though the accuracy is ±0.4% and several sulphide group metals interfere.

Among the other reagents recommended 2-(*o*-hydroxyphenyl)-benzoxazole[3], 1-phenyltetrazoline-5-thione[4] and 1-immino-3-thioisoindoline[5] may be mentioned but all of these have serious limitations due to interference by other metal ions. However N-phenylbenzohydroxamic acid[6] has been reported to be selective in acidic medium.

In this investigation benzoyl-*m*-nitro acetanilide has been used in the gravimetric determination of cadmium. The bis-complex is thermally stable and is quite selective when the diverse ions are masked with sodium- or magnesium-ethylenediamine tetracetate (Na_2-EDTA or Mg-EDTA). The precipitation is instantaneous and filtration is easy.

Experimental

Benzoyl-m-*nitro-acetanilide* : The reagent was prepared[7] by the condensation of ethyl benzoate and *m*-nitroaniline. The reagent has recently been marketed by Polysciences, Inc, U.S.A. Fresh solutions were prepared by dissolving 0.17 to 0.18 of the reagent in 15 ml of aqueous ethanol for each determination.

Cadmium solution : A stock solution was prepared by dissolving hydrated cadmium sulphate (G.R., E. Merck) in dilute sulphuric acid and the metal content was determined using thiourea (Reinecke's salt method[1,2]).

Diverse ion solution : Aqueous solutions of the desired metal ions were prepared from their nitrates, sulphates and chlorides and a little acid was added where necessary.

Magnesium-EDTA solution : Magnesium chloride (0.1 *M*) and Na_2-EDTA (0.1 *M*) solutions were prepared separately and 20 ml portions of each were mixed when required.

Apparatus : A Cambridge *p*H Meter was used for the measurement of *p*H. A photorecording Metriplex Derivatograph OD-102 (Hungary) was used for the thermogravimetric studies.

Procedure : Dilute an aliquot of the stock cadmium (15-25 mg) solution to 200 ml with water and heat on a water bath to 80-90°. Add the alcoholic solution of the reagent (0.17-0.18g) slowly with steady stirring. Adjust the *p*H to 6.8 to 7.8 with aqueous ammonia (2 *M*). Digest the yellow precipitate which was formed immediately on a hot water bath for 20-30 minutes with occasional stirring. Filter the complex through a G4 sintered glass crucible, wash first with hot (80-90°) water and finally with hot aqueous ethanol (30%). Dry at 110-120°. The conversion factor is 0.1656.

When cadmium is to be determined in the presence of diverse ions, add 40 ml of 0.1*M* magnesium-EDTA, before adding the reagent and maintain the final *p*H between 7.0 and 7.5.

The results for the determination of cadmium are given in Table 1.

TABLE 1—DETERMINATION OF CADMIUM

Wt. taken (mg)	Wt. of the complex (mg)	Cd. fouud (mg)	Relative Error (%)
14.0	85.9, 85.9	14.2_2, 14.2_2	+0.15, +0.15
19.6	118.2, 118.6	19.5_7, 19.6_4	−0.15, +0.15
22.4	135.2, 135.6	22.4_0, 22.4_6	nil, +0.26

Results and Discussions

The nature of the complex: The brilliant yellow coloured complex has appreciable solubility in chloroform though practically insoluble in aqueous ethanol. The pure complex dried at 115°, was analysed for the metal content by converting a known weight of it to cadmium sulphate before estimation with thiourea Reinecke's salt method. It was analysed for nitrogen by Duma's method. The results

Found Cd = 26.25% N = 8.1%

Calculated for $Cd(C_{15}H_{11}O_4N_2)_2$ Cd = 16.56%

N = 8.2% indicated the formula of a bis-complex.

Thermogravimetric studied: A known weight of the oven dried complex was mixed with aluminium oxide and heated at the rate of 12° per minute. The complex started decomposing at 310° and this exothermic change was sharp at 410° recording a loss of 35.7% in weight. Another less sharp exothermic change was noted at 515°. Finally, at 900° the total loss in weight was 81.4%. The theoretical loss required for the conversion of $Cd(C_{15}H_{11}O_4N_2)_2$ to CdO is 81.1%.

Optimum p*H and reagent concentration*: Experiments under identical conditions using 19.6 mg of cadmium and 0.18 g of the reagent indicated the precipitation commenced at *p*H 6.5 and was complete between 6.8 and 8.5. At higher *p*H there was some contamination due to the reagent.

In another set of experiments with the same quantity of cadmium and identical precipitation *p*H (7.0), it was observed that after the quantitative precipitation of the complex the supernatant liquid should be at least 0.02% with respect to the reagent.

Effect of sequestering agents: Sulphosalicylate, tartarate and citrate prevented the precipitation of cadmium complex. The precipitation was partial in the presence of ascorbate, iodide and fluoride. However, sodium-or magnesium-EDTA did not interfere in the determination of cadmium with benzoyl-*m*-nitroacetanilide. Magnesium-EDTA was used in preference to sodium-EDTA as a masking agent during separation of cadmium from various other ions as the nature of the $Cd(C_{15}H_{11}O_4N_2)_2$ precipitated was better for filtration than in the presence of Na_2-EDTA.

Effect of diverse ions: Quantitative precipitation of cadmium in the presence of nickel(II), cobalt(II), zinc(II), lead(II), magnesium(II), manganese(II), bismuth(III), aluminium(III), chromium(III) and indium(III) was possible by masking these ions with magnesium-EDTA. The results of these separations are presented in Table 2.

Precision and accuracy: The relative standard deviation of this method was calculated to be ± 0.14% and the 95% confidence limit of the average was 22.35 ± 0.02 mg.

TABLE 2—SEPARATION OF CADMIUM FROM DIVERSE IONS

Cd. taken (mg)	Diverse ion* (mg)	Wt. of complex (mg)	Cd. found (mg)	Rel. error (%)
19.6	Ni^{2+}, 20	117.9, 118.0	19.5_8, 19.5_4	−0.35, −0.30
19.6	Co^{2+}, 20	117.6, 117.8	19.4_7, 19.5_1	−0.52, −0.45
22.4	Zn^{2+}, 25	134.9, 134.9	22.3_5, 22.3_5	−0.22, −0.22
22.4	Pb^{2+}, 25	135.2, 134.9	22.4_0, 22.3_5	nil, −0.22
22.4	Bi^{3+}, 20	135.1, 135.2	22.3_8, 22.4_0	−0.08, nil
19.6	Mg^{2+}, 20	118.1, 118.3	19.5_6, 19.5_9	−0.20, −0.05
19.6	Mn^{2+}, 20	117.9, 117.9	19.5_6, 19.5_6	−0.20, −0.20
19.6	In^{3+}, 20	117.9, 117.6	19.5_6, 19.4_7	−0.20, −0.52
22.4	Cr^{3+}, 20	134.9, 134.9	22.3_5, 22.3_5	−0.22, −0.22
22.4	Al^{3+}, 20	134.8, 134.7	22.3_2, 22.3_1	−0.35, −0.40

* in presence of Mg-EDTA.

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Determination of Silver and Mercury with *p*-(2-Mercaptopropionamido) Benzoic Acid as a Gravimetric Reagent.

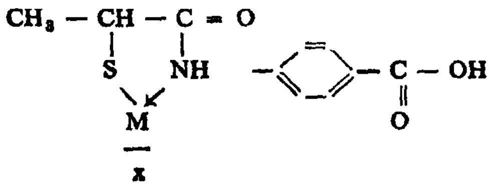
S. V. MUKTIBODH and K. S. BOPARAI

School of Studies in Chemistry, Vikram University, Ujjain.

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p-(2-Mercaptopropionamido) benzoic acid is a selective reagent for the gravimetric determination of Ag(I) and Hg(II) at pH 0.3 to 4.8. The reagent offers the advantages of ease of preparation, keeping qualities in the solid form and solubility in aqueous medium.

MERCAPTOACETAMIDES[1-3] and 2-Mercaptopropionamides[4] are valuable reagents for the determination of some of the sulphide forming metals, however, many of these reagents have the shortcoming of low solubility in water. It was felt that the condensation product of 2-Mercaptopropionic acid and 4-aminobenzoic acid would overcome this shortcoming and might afford quantitative and selective precipitation of some of the cations at low *p*H. The reagent, indeed, fairly meets these requirements. It complexes with the sulphide forming cations to form precipitates which are in most cases soluble in the hot acid medium. Ag(I) and Hg(II) are, however, precipitated quantitatively in the *p*H range 0.3 to 4.8. Cu(II) interferes with their determination but it can be masked with EDTA. As such, the reagent can be used for the selective determinations of Ag(I) and Hg(II). The solubility of the reagent, even at low *p*H, is sufficient so that there is no contamination of the precipitates. The composition of the complexes suggests the following structure[3].



x = Valence of metal M.

Compared to many a organic precipitant[5] which has been thus far reported for the gravimetric determinations of Ag(I) and Hg(II), the use of the present reagent is extremely advantageous in view of its very simple preparation, keeping qualities in the solid form, solubility in aqueous medium and selectivity of reaction.

Experimental

Preparation of the Reagent.

Equimolecular quantities of 2-Mercaptopropionic acid and 4-aminobenzoic acid were refluxed in an atmosphere of carbondioxide at different temperatures ranging between 120° to 170° for different periods of time. Maximum yield of the product was obtained by refluxing for 4½ hours at 140° to 150°. 2-Mercaptopropionic acid (5 ml., Kochlight) and 4-aminobenzoic acid (7.5 g.) were refluxed for 4½ hours by heating in a bath of medicinal paraffin maintained at 140° to 150°. The melt was allowed to solidify and then ground with 25% HCl to remove the unreacted 4-aminobenzoic acid. The crude product weighed 6.6 g. It was recrystallized from benzene-ethanol (2 : 1). The colourless powder melted at 219°-220°, $C_{10}H_{11}O_3NS$ requires: N, 6.22%, S, 14.23%. Found : N, 6.01%, S, 13.82%.

Solutions of Ag(I) and Hg(II)

The solutions were prepared by dissolving AnalaR, B.D.H. samples of silver nitrate and mercuric chloride. Standardization of the solutions was carried out by precipitating as chloride and sulphide respectively. Aliquots were then diluted to prepare 0.15% solutions.

Reagent Solution

Because the solution is susceptible to serial oxidation, fresh solution (0.5%) prepared by dissolving the required amount of the solid in hot ethanol and diluting with 9 parts of hot water was used.

Procedure for the Determination of Ag(I) and Hg(II)

Twenty ml. of the solution of the cation to be estimated was taken in a beaker and diluted to about 125 ml. Required amount of 2 *N* nitric acid in the case of silver and 2 *N* hydrochloric acid in the case of mercury was introduced to adjust the *p*H at 1 to 2. The solution was heated on a steam bath and the reagent solution was introduced dropwise with constant stirring. The precipitate, thus obtained, was digested for about 45 minutes, filtered through a sintered glass crucible G 3, washed with hot water to remove any adhering reagent, dried to a constant weight at 110°

TABLE 1 – DETERMINATION OF Ag(I) AND Hg(II) IN PRESENCE OF DIVERSE IONS. (30 mg. OF THE METALS TAKEN FOR THEIR RESPECTIVE DETERMINATIONS).

Diverse ion	Amount added mg.	Wt. of Ag complex mg.	Ag found mg.	Error mg.	Wt. of Hg complex mg.	Hg Found mg.	Error mg.
—	—	92.0	29.90	−0.10	97.2	30.04	+0.04
—	—	91.8	29.84	−0.16	97.0	29.98	−0.02
—	—	92.4	30.03	+0.03	97.0	29.98	−0.02
—	—	92.4	30.03	+0.03	97.0	29.98	−0.02
Na(I), K(I)	100	92.8	30.15	+0.15	96.0	29.67	−0.3
NH_4(I)	100	92.0	29.90	−0.10	96.8	29.92	−0.08
Ca(II), Ba(II)	100	92.4	30.03	+0.03	96.8	29.92	−0.08
Sr(II), Mg(II)	100	92.4	30.03	+0.03	97.2	30.04	+0.04
Zn(II)	100	92.4	30.03	+0.03	97.0	29.98	−0.02
Mn(II)	100	92.8	30.15	+0.15	97.0	29.98	−0.02
Co(II)	100	92.4	30.09	+0.09	97.0	29.98	−0.02
Ni(II)	100	92.6	30.32	+0.23	97.6	30.16	+0.16
Al(III)	100	93.0	30.23	+0.23	97.6	30.16	+0.16
Cr(III)	100	92.6	30.09	+0.09	98.0	30.29	+0.29
Fe(III)	100	91.4	29.70	−0.30	97.0	29.98	−0.02
As(III)	100	—	—	—	97.0	29.98	−0.02
Sb(III)	100		—	—	97.2	30.04	+0.04
Cd(II)	100	92.4	30.03	+0.03	97.0	29.98	−0.02
Pb(II)	100	92.0	29.90	−0.10	96.6	29.86	−0.14
Bi(III)	100	93.0	30.23	+0.23	97.2	30.04	+0.04
Cu(II)[a]	50	92.8	30.15	+0.15	97.2	30.04	+0.04
Tl(I)	25	92.0	29.90	−0.01	96.8	29.92	−0.08
Th(IV)	25	92.4	30.03	−0.03	97.0	29.98	−0.02
Zr(IV)	25	92.4	30.03	+0.03	96.8	29.92	−0.08
UO_2(II)	25	92.6	30.09	+0.09	97.2	30.04	+0.04
VO(II)	25	92.4	30.03	+0.03	97.2	30.04	+0.04
Ce(IV)	25	92.8	30.15	+0.15	96.6	29.86	−0.14
Molybdate[b]	50	92.4	30.03	+0.03	96.8	29.92	−0.08
Tungstate[b]	50	92.4	30.03	+0.03	97.2[c]	30.04	+0.04

[a] Masked with EDTA at *p*H 4.8.

[b] In the determination of silver in the presence of molybdate and tungstate, EDTA was used at *p*H 4.8 to prevent the precipitation of the corresponding salts.

[c] The determination was carried out at *p*H 4.8.

and weighed. The weights of the complexes multiplied by 0.3250 and 0.3090 give the weights of silver and mercury respectively.

Determinations in the Presence of Diverse Ions

Alkali metals, alkaline earths, ammonium, Zn(II), Mn(II), Co(II), Ni(II), Al(III), Cr(III), Fe(III), Cd(II), Pb(II), Bi(III), Tl(I), Th(IV), Zr(IV), VO(II), UO_2(II), molybdate and tungstate do not interfere with the determinations of Ag(I) and Hg(II). The interference due to Cu(II) can be prevented by masking it with EDTA. In the determination of silver in the presence of molybdate and tungstate, EDTA prevents the precipitation of the corresponding salts. Though the determination of mercury in the presence of Sb(III) and As(III) was carried out, that of silver in their presence was not possible because these cations were available only as chlorides.

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Solvent Sensitized Dye Interaction Technique for End Group Analysis of Acrylonitrile Polymers. Part II—Verification by Calculation of r_1 in Acrylonitrile Copolymers.

C. KANJILAL, B. C. MITRA, A. K. BANTHIA and S. R. PALIT

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032.

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Based on a newly developed solvent sensitized dye interaction technique (SSDIT) for the determination of carboxyl groups in acrylonitrile polymers, the copolymer reactivity ratio (r_1) for the following pairs of monomers (1) acrylonitrile (M_1)—acrylic acid(M_2); (2) acrylonitrile (M_1)-sodium acrylate (M_2); (3) acrylonitrile (M_1)-methacrylic acid (M_2); (4) acrylonitrile (M_1)-maleic anhydride (M_2); (5) acrylonitrile (M_1)-crotonic acid (M_2); at varying M_1 : M_2 ratios (100 : 1 to 1000 : 1), were determined. The experimental r_1 values compare reasonably well with the literature values where known. This proves the validity of the SSDIT for the estimation of carboxyl groups in acrylonitrile polymers.

A solvent sensitized dye interaction technique[1] (SSDIT) has recently been developed for the estimation of carboxyl end groups in acrylonitrile polymers. Copolymers of acrylonitrile (M_1) as predominant monomer and other carboxyl bearing monomers (M_2) e.g., acrylic acid, sodium acrylate, etc., have been prepared and the monomer reactivity ratio r_1 has been determined by measuring the carboxyl group content in those copolymers by using the equation (1)[2,3] :

$$\lim_{(M_2/M_1)_f \to 0} \frac{(M_2/M_1)_f}{(M_2/M_1)_p} = r_1 \qquad (1)$$

where $(M_2/M_1)_f$ and $(M_2/M_1)_p$ represent the molar ratio of the component monomers M_1 and M_2 in the feed and copolymer respectively. A comparison of the experimental r_1 values with the literature values will thus verify the quantitative accuracy obtainable by the present method[1].

Experimental

Acrylonitrile was purified by the usual procedure. Acrylic acid and methacrylic acid were purified by freezing them several times in a refrigerator and finally by distillation under reduced pressure in presence of a copper salt. The major middle fraction was always used. Sodium acrylate[4] was prepared by titration of acrylic acid to neutrality (*p*H-7.0) which corresponds to 99% of sodium acrylate.

Purification of N,N-dimethylformamide (DMF) was described elsewhere[1]. Benzene (thiophene free), methanol and petroleum ether were freshly distilled before use.

Preparation and Purification of Copolymers: The copolymers of acrylonitrile (M_1) and other carboxyl bearing monomers (M_2) were prepared both in aqueous and non-aqueous (DMF) medium at varying M_1 : M_2 ratios in the composition range 100 : 1 to 1000 : 1. In aqueous medium, the polymerization was achieved in an atmosphere of nitrogen using the initiating system Fe^{2+}-H_2O_2 or, H_2O_2-u.v. at desired temperatures. Copolymers with different ratios of the monomers were obtained for acrylonitrile-acrylic acid, acrylonitrile-sodium acrylate, acrylonitrile-methacrylic acid pairs. The conversion of monomers in all cases was limited to 10-15%. The copolymer precipitated on formation was filtered, washed free from iron and dried under vacuum. The polymerization in DMF was carried out with benzoyl peroxide (Bz_2O_2) as initiator in vacuum sealed pyrex glass tubes at desired temperatures to low conversion. Copolymers with different ratios of the monomers were obtained for acrylonitrile-acrylic acid, acrylonitrile-methacrylic acid, acrylonitrile-maleic anhydride, acrylonitrile-crotonic acid, pairs. Polymers were precipitated from their viscous solutions with cold methanol.

The copolymers were rigorously purified by reprecipitation with cold methanol from their DMF solutions, cold methanol was selected as the precipitant

since this was not a nonsolvent for the homopolymers of the co-monomers used in the present study but it precipitated quantitatively both polyacrylonitrile and acrylonitrile copolymers from their DMF solutions. As the presence of methanol might affect the dye interaction, test (SSDIT) the copolymers were, after rigorous purification, washed with petroleum ether for four or, five times to remove any trace of methanol. These purified polymers were finally dried under vacuum.

Preparation of the Dye-Reagent : The methylene-blue MT dye reagent was obtained by immediate extraction from an approximately 0.4% strong caustic soda solution of the dye (8-10 mg. in 5 ml) with 100 ml. of thiophene free pure benzene[1]. This red coloured dye extract was then stored over solid caustic soda in dark.

Determination of the Copolymer Composition from SSDIT : The resulting polymers were subjected to solvent-sensitized dye interaction test (SSDIT) for the evaluation of the composition of the copolymers. This was done by preparing solutions of the copolymers in such a manner that the approximate carboxyl content in the solutions lay within the concentration range of 1.0×10^{-5} mol.l.$^{-1}$ to 1.0×10^{-4} mol.l.$^{-1}$. In each case, all the copolymers were dissolved in 3 ml of DMF and 2 ml of the benzene extract of the Methylene Blue MT dye reagent[1] was used. The O.D.'s of the resulting polymer solution in benzene-DMF mixed solvent were measured at 650 mμ with the Hilger Uvispek Spectrophotometer and were compared with the calibration curve obtained with a standard polymeric acid as well as cyanoacetic acid[1].

Results and Discussion

The experimental results for the copolymerisations studied are presented in Table-1, and their graphical representations are shown in the Figs. 1 to 3. The

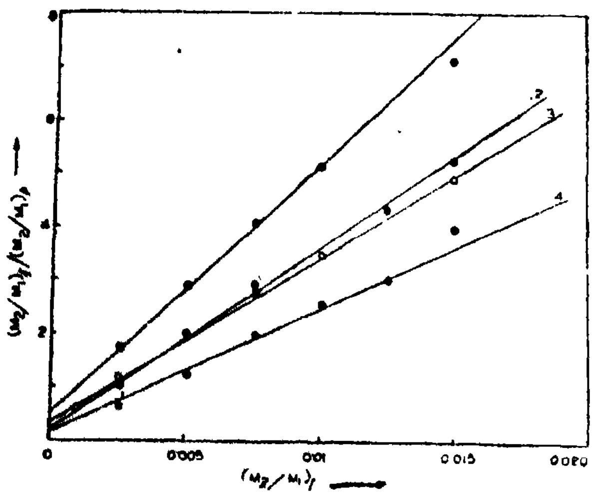


Fig. 1. Plot of $(M_2/M_1)_f/(M_2/M_1)_p$ against $(M_2/M_1)_f$ for copolymers to determine r_1.
1. acrylonitrile (M_1)-acrylic acid (M_2) ; 30°C,
2. acrylonitrile (M_1)-sodium acrylate (M_2) ; 50°C,
3. acrylonitrile (M_1)-acrylic acid (M_2) ; 50°C,
4. acrylonitrile (M_1)-sodium acrylate (M_2) ; 30°C.

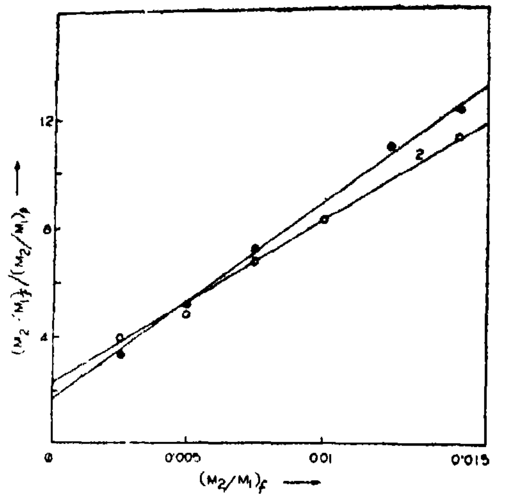


Fig. 2. Plot of $(M_2/M_1)_f/(M_2/M_1)_p$ against $(M_2/M_1)_f$ for copolymers to determine r_1 in acrylonitrile (M_1)-methacrylic acid (M_2) copolymerization 1. 60°C, 2. 30°C.

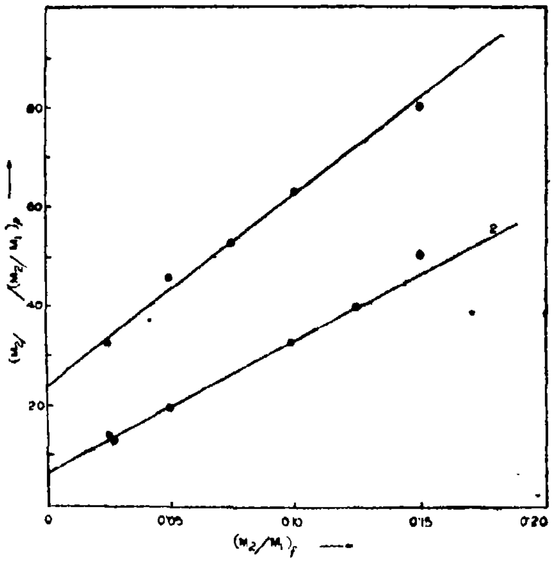


Fig. 3. Plot of $(M_2/M_1)_f/(M_2/M_1)_p$ against $(M_2/M_1)_f$ for copolymers to determine r_1.
1. acrylonitrile (M_1)-crotonic acid (M_2) ; 60°C,
2. acrylonitrile (M_1)-maleic anhydride (M_2) ; 60°C.

monomer reactivity ratio r_1 for each monomer pair was calculated by the application of equation (1). For each copolymer $(M_2/M_1)_f/(M_2/M_1)_p$ values were plotted against respective $(M_2/M_1)_f$ values. The plots, in general, followed a straight line. The r_1 value of the copolymer concerned was given by the intercept obtained by extrapolation of this straight line to zero value of $(M_2/M_1)_f$. The estimation of the copolymer composition, i.e. $(M_2/M_1)_p$ was done with the help of the newly developed solvent sensitized dye interaction test by the determination of the carboxyl content in the polymer. Cyanoacetic acid and polyacrylonitrile were taken as the basis of comparison.

TABLE 1—COPOLYMER COMPOSITION AND MONOMER REACTIVITY RATIOS AS DETERMINED BY THE SOLVENT SENSITIZED DYE INTERACTION TECHNIQUE (SSDIT).

Copolymer	$(M_2/M_1)_f$	Condition of polymerisation	% concn. of polymer solution	Optical density at 650 mμ	Corresponding concn. from calibration curve $\times 10^5$	$(M_2/M_1)_p$ $\times 10^3$	$\frac{(M_2/M_1)_f}{(M_2/M_1)_p}$	r_1 values experimental	r_1 values Literature
Acrylonitrile (M_1)	0.0025	Aqueous. 30°C	0.100	0.308	2.75	1.461	1.711		
Acrylic acid (M_2)	0.0050	H_2O_2 – u.v.	,,	0.354	3.30	1.755	2.850		
		0.08 m/l							
	0.0075		,,	0.372	3.50	1.850	4.053	0.50	—
	0.0100		,,	0.387	3.70	1.955	5.113		
	0.0150		,,	0.408	3.95	2.105	7.127		
Acrylonitrile (M_1)	0.0010	Aqueous, 50°C	0.100	0.342	3.15	1.661	0.602		
Acrylic acid (M_2)	0.0025	Fe^{+2}(2.5 ×	,,	0.421	4.10	2.178	1.148		
	0.0075	10^{-4} m/l) –	,,	0.509	5.15	2.727	2.751	0.36	0.35 (5)
	0.0100	H_2O_2(0.04 m/l)	,,	0.534	5.45	2.879	3.473		
	0.0150		,,	0.562	5.78	3.062	4.899		
Acrylonitrile (M_1)	0.0050	Non-aqueous	0.050	0.402	3.87	4.099	1.220		
	0.0075	DMF, 80°C	,,	0.381	3.63	3.845	1.951		
	0.0100	Bz_2O_2	,,	0.395	3.77	3.997	2.502	0.15	0.13±0.02
Acrylic acid (M_2)	0.0125	(4.0 × 10^{-3}m/l)	,,	0.406	3.93	4.164	3.003		
	0.0150		,,	0.380	3.62	3.839	3.907		(6)
Acrylonitrile (M_1)	0.0025	Aqueous, 50°C	0.100	0.452	4.48	2.376	1.052		
Sodium acrylate (M_2)	0.0050	H_2O_2(0.04 m/l)	,,	0.476	4.75	2.513	1.990		
	0.0075	Fe^{+2}(2.5 × 10^{-4})	,,	0.484	4.85	2.579	2.908	0.20	0.21
	0.0125	m/l)	,,	0.534	5.45	2.894	4.320		
	0.0150		,,	0.530	5.40	2.856	5.252		(5)
Acrylonitrile (M_1)	0.0025	Aqueous, 30°C	0.100	0.176	1.22	0.6427	3.890		
Methacrylic acid (M_2)	0.0050	H_2O_2 – u.v.	,,	0.245	2.00	1.062	4.708		
	0.0075	(0.08 m/l)	,,	0.258	2.15	1.137	6.595	2.22	—
	0.0100		,,	0.270	2.30	1.221	8.188		
	0.0150		,,	0.289	2.53	1.340	11.20		
Acrylonitrile (M_1)	0.0025	DMF medium	0.100	0.200	1.45	0.7672	3.258		
Methacrylic acid (M_2)	0.0050	60°C, Bz_2O_2	,,	0.232	1.83	0.9692	5.160		
	0.0075	(2.0 × 10^{-3} m/l)	,,	0.244	1.98	1.049	7.151	1.68	—
	0.0125		,,	0.258	2.15	1.148	10.89		
	0.0150		,,	0.270	2.30	1.227	12.23		
Acrylonitrile (M_1)	0.025	DMF medium	0.100	0.200	1.45	0.7686	32.52		
Crotonic acid (M_2)	0.050	60°C, Bz_2O_2	,,	0.249	2.05	1.085	46.08		
	0.075	(4.0 × 10^{-3} m/l)	,,	0.303	2.70	1.430	52.47	23.8	21.0±10
	0.100		,,	0.328	3.00	1.586	63.05		
	0.150		,,	0.373	3.53	1.873	80.11		(7)
Acrylonitrile (M_1)	0.025	DMF medium	0.100	0.358	3.35	1.769	14.13		
Maleic anhydride (M_2)	0.050	60°C, Bz_2O_2	,,	0.478	4.78	2.535	19.50		
	0.100	(4.0 × 10^{-3} m/l)	,,	0.563	5.80	3.078	32.49	6.5	6.0
	0.125		,,	0.572	5.90	3.116	40.12		
	0.150		,,	0.548	5.62	2.977	50.40		(8)

Figures shown within brackets in the last column indicate references.

It may be observed that the results of the r_1 values presented in the Table-1 (obtained on the basis of the introductory assumptions) are found to compare reasonably well with most of the available values given in the literature. This produces an evidence in favour of the present method in regard to the order of attainable accuracy for the determination of end groups in polymers.

There might have been some doubt in the quantitative aspect of the method, had it been only cyanoacetic acid as the sole basis of comparison for the calculation of r_1 values for the copolymers. This suspicion, however, has been mostly removed by using polyacrylonitrile with known carboxyl content for calibration[1]. It may be metioned in this connection that both of them give the same calibration curve[1]. The r_1 values for the copolymer of acrylonitrile with methacrylic acid could not be checked from the literature. However, from the fair agreement of most of the experimental r_1 values with the existing literature values, it may be quite logically concluded that the present dye interaction method gives a fairly reasonabl estimate of the carboxyl content in acrylonitril copolymers.

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Redox Titrations in Non-aqueous Solvents. Determination of Mercaptans, Dithiocarbamates and Xanthates

KRISHNA K. VERMA, JAMEEL AHMED, M. P. SAHASRABUDDHEY and SAMEER BOSE

Department of Chemistry, Government Science College, University of Jabalpur, Jabalpur 482001

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Titrimetric procedures, with a visual or potentiometric control of the end point, are described for the determination of mercaptans with iodine monochloride, iodine trichloride, iodobenzene dichloride and N-bromosuccinimide in a mixed solvent of acetonitrile-methanol, and with iodine cyanide, diacetoxy iodobenzene and chloramine-T in acetic acid-methanol. Dithiocarbamates and xanthates are determined with iodine monochloride, iodine trichloride and iodobenzene dichloride in acetonitrilemethanol. Non-aqueous solutions of the oxidizing agents are stable. The procedures are rapid and accurate to 0.1% with a precision of 0.2%. Hydrogen sulphide and thiocarbonyl compounds interfere. Methanol accelerates the oxidation which is otherwise slow in anhydrous acetic acid or acetonitrile. A molecular complex that is formed in the latter solvents is supposed to be broken by methanol.

THE number of redox titrations in non-aqueous media for the determination of organic compounds via functional groups is relatively small. The realization of the theoretical possibilities offered by non-aqueous solutions is reflected by the great variety of acid-base titrations in such media. The use of non-aqueous solvents as media for redox titrations is limited by the lack of oxidizing titrants of suitable stability. The availability of such titrant-solvent systems will lead to the employment of redox titrations for compounds insoluble or unstable in aqueous medium.

The present work was undertaken with a view to test the applicability of some oxidizing agents in the determination of certain sulphur-containing functional groups in non-aqueous solvents. The determination of mercaptans with cupric oleate in 1933 by Bond[1] was probably the first non-aqueous redox titration. This method was later modified by Turk and Reid[2] who employed cupric alkyl-phthalates in hydrocarbons. Use is also made of cupric perchlorate in acetonitrile to titrate thiourea and ethyl xanthate[3,4], of cupric sulphate in dimethylformamide and ferric chloride in pyridine for some mercaptans[5]. Cupric, chromate, ferric and mercuric ions in dimethylformamide solutions have been evaluated for their analytical potential[6]. Lead tetraacetate in anhydrous acetic acid was used for the determination of mercaptans[7,8] and phenyl thioureas[9]. Acetonitrile solution of ammonium ceric nitrate was found suitable to titrate xanthates[10] and thiourea and its alkyl derivatives[11]. Recently, N-bromosuccinimide is used in acetonitrile for xanthates and dithiocarbamates[12].

In the present paper, procedures are given for the use of iodine monochloride, iodine trichloride and iodobenzene dichloride in acetonitrile-methanol for the determination of mercaptans, dithiocarbamates and xanthates. Diacetoxy iodobenzene, iodine cyanide and chloramine-T in acetic acid-methanol are used for titrating mercaptans. Acetonitrile and anhydrous acetic acid, owing to their inertness towards oxidizing and reducing agents, are solvents of choice. Methanol can be used as a cosolvent when the oxidizing agent does not react with it.

Experimental

Reagents :

Iodine monochloride, 0.05N solution in acetonitrile, was prepared by dissolving an approximate amount of the commercially available sample.

Iodine trichloride, 0.05N solution in acetonitrile, was prepared by dissolving an approximate amount of the commercially available sample.

Diacetoxy iodobenzene, 0.05N solution in anhydrous acetic acid, was prepared by the method of Pausacker[13].

N-Bromosuccinimide, 0.05N solution in acetonitrile, was prepared by dissolving with stirring ca. 4.5 g of sample per litre. The insoluble portion of the reagent was filtered off. The solution was kept in the dark.

Iodobenzene dichloride, 0.05N solution in acetonitrile, was prepared by the method as described by Vogel[14].

Chloramine-T, 0.05N solution in methanol, was prepared by dissolving ca. 5.7 g of sample per litre.

Iodine cyanide, 0.05N solution in acetonitrile, was prepared by dissolving ca. 3.8 g of sample[18] per litre. All these oxidant solutions were standardised iodometrically.

Samples :

Most of the mercaptans were received from Messrs Evans Chemetics, New York, and were used as such.

Diethyldithiocarbamate was a commercial product, the rest being prepared by the usual methods[16,17].

Xanthates were prepared from the corresponding sodium or potassium alkoxide by reaction with carbon disulphide[18]. The product was recrystallized by dissolution in acetone, filtration of any insoluble matter, and precipitation by adding petroleum ether to the filtrate.

All solvents used were reagent grade chemicals.

Procedures :

Tritration of mercaptans : A sample containing 0.1-1.0 mequiv of mercapto group is weighed in a 150-ml Erlenmeyer flask containing 30 ml of methanol. When diacetoxy iodobenzene, N-bromosuccinimide, chloramine-T, iodobenzene dichloride or iodine trichloride is used as the titrant, about 50 mg potassium iodide is added and the contents of the flask are swirled to dissolve the solid. About 0.5 ml of anhydrous acetic acid is also added when chloramine-T and iodine cyanide are being used. Titration is followed with 0.05N solution of any of above reagents or iodine monochloride, taken in a 10-ml burette graduated to 0.02 ml. The end-point is indicated by the appearance of iodine colour formed by the first drop in excess of the oxidizing agent by reaction with potassium iodide. Sufficient methanol is to be added so that it is about 80% of the total solvent at the end-point.

In potentiometric titrations, the sample is taken in a 100-ml beaker and the procedure for adding reagents is the same. A modified calomel or antimony electrode is used as the reference electrode and a bright platinum wire as the indicator electrode. The end-point is shown by a large potential jump.

Titration of dithiocarbamates and xanthates : A sample is weighed containing 0.1-1.0 mequiv of -CS.SK group and dissolved in 30 ml of methanol. About 50 mg of potassium iodide is added when iodine trichloride or iodobenzene dichloride is used as the titrant. Titration is followed with 0.05N solution of any of the above reagents or iodine monochloride, being delivered from a 10-ml burette graduated to 0.02 ml, to the appearance of iodine colour. Methanol should be about 80% of the total solvent at the end-point.

The method of potentiometric titration is the same as described for mercaptans.

Results and Discussion

Under the described conditions of titration, mercaptans are oxidized to disulphides, dithiocarbamates to thiuram disulphides and xanthates to dixanthogens. Results are given in Table 1 for the determination of mercaptans. The results obtained with seven titrants are compared with those found by mercurimetry[19], lead(IV) titration[8], alkalimetry[20], iodimetry[21] and copper(II) titration[2]. Table 2 includes the results on the determination of dithiocarbamates and xanthate with three titrants. Results for the purity determination of dithiocarbamates are compared with those obtained by mercurimetry[22] and of xanthates by argentimetry[23]. From the pooled data it is found that the present methods furnish results which are precise in the range 0.1-0.2%. The results agreed within 0.1% with those found by comparison methods.

TABLE 1—DETERMINATION OF MERCAPTANS

Compound	Purity, % Present methods[a]								Comparison method
	ICl_3	Chloramine-T	ICl	NBS	$PhI(OAc)_2$	ICN	$PhICl_2$		
Benzenethiol	98.5	—	—	98.6	98.3	—	98.5	98.4	Alkalimetry
2-Naphthalenethiol	–	99.7	99.9	99.5	–	99.6	–	99.6	Alkalimetry
2-Mercaptoethanol	97.5	97.3	97.3	97.4	97.6	97.4	97.5	97.3	Pb^{4+} titration
2-Mercaptopropionic acid	–	95.2	—	95.0	95.4	—	–	95.5	Hg^{2+} titration
Mercaptoacetic acid	92.6	92.8	93.0	—	—	—	92.7	92.9	Iodimetry
p-Toluenethiol	—	—	99.7	99.5	—	99.3	—	99.6	Cu^{2+} titration
p-Chlorobenzenethiol	98.0	97.8	—	98.2	98.5	—	—	98.1	Alkalimetry
2-Mercaptoethylamine	—	95.1	–	95.4	—	—	95.3	95.2	Iodimetry
1-Butanethiol	98.5	98.2	98.0	98.5	98.1	98.0	98.2	98.3	Cu^{2+} titration
2-Diethylaminoethanethiol	—	99.6	99.4	—	99.4	—	—	99.5	Pb^{4+} titration
Toluene-α-thiol	97.5	—	—	97.2	97.1	—	97.0	97.2	Cu^{2+} titration
Glycerol-1-thiol	79.1	79.5	79.3	79.0	79.2	79.3	79.3	79.3	Iodimetry

[a] Average of 10 determinations.

Organic disulphides, sulphides, *p*-aminobenzoic and p-hydroxybenzoic acids do not interfere with the procedures. Large amounts (1 mole of reductant : 100 moles of added substance) of carbon disulphide, formic acid and dimethylsulphoxide do not interfere. Thiophene (1 : 18), acetaldehyde (1 : 12) and acetone (1 : 4) cause about 1% high results. Acrylonitrile (1 : 250) gives 1% low results. Serious interference is caused by thiourea and hydrogen sulphide.

In acetonitrile or anhydrous acetic acid alone, or in their mixtures, the reactions are slow and iodine appears during the course of titration In methanol or in its mixtures with acetonitrile or anhydrous acetic acid containing about 80% of methanol at the end-point, the reactions are instantaneous and the end point can be located accurately. The dependence of oxidation on methanol is apparently environmental rather than stoichiometric.

Danehy[24], from a spectrophotometric study, has found that when the ratio of thiol to iodine in glacial acetic acid is sufficiently high the absorption due to iodide is all but completely extinguished and is replaced by a much more intense absorption both in the near ultraviolet and the near infrared. This corresponds to observations in acetonitrile also. It is not the sulphenyl iodide that is formed, as such substances are intensely coloured. The possibilities of the formation of a charge transfer complex between thiol and iodine or initially formed disulphide and iodine, are consistent with the prevailing information on charge transfer complexes of iodine with many compounds.

1. $RSH + I_2 \rightleftharpoons RSH.I_2$

2. $2RSH + I_2 \rightleftharpoons RSSR + 2HI$

$RSSR + I_2 \rightleftharpoons RSSR.I_2$

The effect of methanol in promoting the oxidation can be attributed to its basicity which is responsible for decomposing the molecular complex and for inhibiting the protonation of iodide ion.

$$RSH + I_2 \xrightarrow{MeCN} \begin{matrix} R \\ H \end{matrix}\!\!>\!S \rightarrow I_2$$

$$\begin{matrix} R \\ H \end{matrix}\!\!>\!S \rightarrow I_2 + MeOH \underset{MeOH}{\overset{MeCN}{\longleftrightarrow}} [RSI_2]^- \xrightarrow{fast} RSI + I^- + MeOH_2^+$$

$$MeOH_2^+ + I^- \rightarrow HI + MeOH$$

$$RSI + RSH \underset{MeOH}{\overset{MeCN}{\longleftrightarrow}} RSSR + HI$$

If it is the basicity of methanol that breaks the molecular complex and promotes the oxidation then a more basic species could also fulfil the purpose. A reference may be given here of a method that uses pyridine as a catalyst in the titration of some thiols with iodine in benzene medium[25].

Dithiocarbamates and xanthates are decomposed by acids to the corresponding amines and alcohols respectively together with carbon disulphide. Because of its solution in acetic acid, diacetoxy iodobenzene could not be used for these compounds. The determination can, however, be made feasible if the reagent solution is prepared in acetonitrile. Chloramine-T and iodine cyanide function only in acidic medium and, therefore, are inapplicable.

All of the reagents used in these studies are of good stability in non-aqueous media. Unlike aqueous solution, N-bromosuccinimide in acetonitrile does not liberate molecular bromine even if stored for 5 days at 20°.

TABLE 2—DETERMINATION OF DITHIOCARBAMATES AND XANTHATES

Compounds	Purity, % Present methods[a]			Comparison method	
	ICl_3	$PhICl_2$	ICl		
Diethyldithiocarbamate	75.9	76.0	—	76.3	Hg^{2+} titration
Di-isopropyldithiocarbamate	—	87.5	87.2	87.0	Hg^{2+} ,,
Di-n-butyldithiocarbamate	91.3	91.0	91.5	91.4	Hg^{2+} ,,
Phenylethyldithiocarbamate	—	79.7	79.8	80.0	Hg^{2+} ,,
Diamyldithiocarbamate	92.0	91.8	92.2	92.1	Hg^{2+} ,,
1-Propylxanthate	97.8	—	98.0	98.1	Ag^+ ,,
Ethylxanthate	90.4	90.2	—	90.0	Ag^+ ,,
1-Butylxanthate	—	94.6	94.4	94.8	Ag^+ ,,
Allylxanthate	—	94.4	94.8	94.5	Ag^+ ,,
Isopropylxanthate	77.7	78.0	—	78.2	Ag^+ ,,
Isoamylxanthate	95.5	—	95.2	95.0	Ag^+ ,,
1-Octylxanthate	—	97.0	97.1	97.3	Ag^+ ,,

[a] Average of 8 determinations

Chloramine-T loses titre rapidly in anhydrous acetic acid but is stable in methanol. Iodine monochloride, iodine cyanide and iodine trichloride can be kept indefinitely. Iodobenzene dichloride requires standardization daily and diacetoxy iodobenzene is to be checked after every 3 days.

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Intramolecular Kinetic Isotope Fractionation in the Decomposition of Alkaline Earth Carbonates by 47% Aqueous Hydrobromic Acid. Part II.

R. C. JHA and LALLAN SINGH*

Department of Chemistry, Patna University, Patna-800005.

and

T. SHARMA

Department of Chemistry, L. S. College, Muzaffarpur.

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The intramolecular kinetic oxygen isotope fractionation factor, ∝ in the decomposition of the carbonates of strontium and barium by 47% aq. HBr has been determined at temperatures ranging from 25° to 62°. The values have been found to decrease with increase of temperature which has been attributed due to the loosening of the C–O bonds. An empirical relationship between 1000 ln∝ and temperature has been suggested. The increase of ∝ values with increasing mass of cation of the carbonates has been explained on the basis of the increasing ionic character of the alkaline earths.

A previous paper in this series[1] described the decomposition of calcium carbonate by 47% aq. HBr in the temperature range 25°–62°, the comparison of the kinetic isotope fractionation factor, ∝ with that obtained by 100% phosphoric acid and the empirical relationship between the fractionation factor, ∝ and the temperature of decomposition of the carbonate samples of calcium. In the same continuation the present investigation deals with the determination of ∝ values of the different samples of the carbonates of strontium and barium in the same temperature range with a view to examine the effect of temperature and mass of the cation of the carbonates on the isotopic fractionation factor, ∝. The possibility of using 47% aq. HBr for the decomposition of the carbonate minerals in preference to the use of 100% phosphoric acid has also been explored.

Experimental

Several carbonate samples of strontium and barium were decomposed by 100% phosphoric acid at 25° by the method described by Sharma et. al.[2] and Singh et. al.[3,4] The same samples were also decomposed by 47% aq. HBr at 25°, 30°, 45°, 55° and 62°. The procedure adopted was same of that in our previous communication[1]. The carbon dioxide evolved was transferred in sample tubes for mass spectrometric analysis, which was carried out on a 6″–60°–RMS–19 double collecting isotope ratio mass spectrometer designed after Neir[5] and Mckinney et. al.[6] in the department of chemistry, I. I. T, Kanpur. The isotope ratio variations has been expressed in terms of δ, where

$$\delta = \left[\frac{(O^{18}/O^{16})\ \text{sample}}{(O^{18}/O^{16})\ \text{standard}} - 1\right] \times 1000$$

The kinetic fractionation factor, ∝ is calculated using the relationship,

$$\alpha = \frac{1+\delta CO_2/1000}{1+\delta CO_3^{=}/1000}$$

in the same way as in our previous papers.

Results and Discussion

Table 1 shows the δ values of carbon dioxide as well as the carbon dioxide yield when the sample were decomposed by 100% phosphoric acid at 25°C. The table also includes the $\delta CO_3^{=}$ values calculated on the basis of fractionation factor reported in literature[7]. The carbon dioxide yield and δO^{18} values of carbon dioxide obtained by the decomposition with 47% aq. HBr at the temperature range 25–62° have been presented in table 2. Comparing the carbon dioxide yield of the samples with the theoretically expected yield (6.77 μ moles for $SrCO_3$ and 5.00 for $BaCO_3$) it is evident that the samples have nearly 99% of purity.

* For correspondence

TABLE 1—$\delta CO_3^=$ VALUES CALCULATED FROM δCO_2 OBTAINED BY 100% H_3PO_4 METHOD AT 25°C.

Carbonate	Sample	CO_2 yield in μ moles/mg	δCO_2	Calculated $\delta CO_3^=$
	S B 1	6.63	1.34	−8.87
$SrCO_3$	S B 2	6.70	4.13	−6.11
	S B 3	6.71	5.50	−4.75
	S B 4	6.66	6 90	−3.36
	B C 1	4.92	14.37	3.55
$BaCO_3$	B C 2	4.95	14.64	3 82
	B C 3	4.93	12.15	1.35
	B C 4	4.97	13.27	2 46

Table 3 shows the enhancement of α values with increasing atomic weight of the metal of the carbonates. This may be explained on the increasing ionic character of the metal atom. As the ionic character increases, the covalent character decreases and the valence electron of the metal is relatively more transferred towards the carbonate ion which strengthens the C−O bond. For a strong C−O bond the lighter isotope is decomposed comparatively faster than the heavier isotope, resulting an increase in the α value. Thus the strength of C−O bond in decreasing order in the alkaline earth carbonates is as $BaCO_3 > SrCO_3 > CaCO_3$[1].

TABLE 2—δCO_2 VALUES FOR $SrCO_3$ and $BaCO_3$ OBTAINED BY 47% aq. HBr method.

Temp°C	δCO_2 for $SrCO_3$ SB1	SB2	SB3	SB4	δCO_2 for $BaCO_3$ BC1	BC2	BC3	BC4
25	−0.34	2.46	3 85	5.24	12.64	12.93	10.43	11.55
30	−0.47	2.33	3.72	5.11	12.51	12 80	10 30	11.43
36	−0.63	2.17	3.55	4.94	12.35	12 63	10.15	11.26
45	−0.91	1.88	3.23	4.63	12.12	12.39	9.91	11.03
55	−1.21	1.58	2.96	4.35	11.85	12 12	9.63	10.75
62	−1.39	1.39	2.77	4.16	11.66	11.93	9.44	10.56
CO_2 yield μ moles/mg	6.64	6.68	6.70	6.67	4.94	4.93	4.95	4.96

The investigation of intramolecular kinetic fractionation factor α using 47% aq. HBr in the decomposition of alkaline earth carbonates, indicates the possibility of this method to be used in the analysis of O^{18}/O^{16} ratio variation in carbonate minerals. The α values, depicted in the form of 1000 ln α, for different samples of carbonates of Sr and Ba are shown in table 3. It is quite evident from the above as well as the previous result[1] that α values for a particular carbonate at a particular temperature is almost constant. The error in the measurement is in the fifth place of decimal and therefore it is not affecting the constancy of the α values. The values of αHBr is as precise as that of αH_3PO_4 obtained by Sharma and Sharma[7]. Therefore, in preference to the 100% H_3PO_4 readily available 47% aq. HBr can be safely used in the analysis of O^{18}/O^{16} variation in carbonate minerals. The only difficulty encountered in the process is to check the copious fumes of HBr during evacuation, which is achieved by coling the reaction vessel to ice temperature.

The cause for decrease in the values of α with temperature has been attributed to the loosening of C−O bond. With the increase in temperature the C−O bond loosens and so the decomposing reagent finds less distinction between $C-O^{16}$ and $C-O^{18}$ bonds to break and therefore k_1, the rate coefficient of decomposition of $C-O^{16}$ bond tends to k_2, the rate coefficient of $C-O^{18}$ bond. Since $\alpha = \frac{3k_1}{k_1+k_2}$, the values of α decreases with the decrease in the values of k_1 and ultimately at infinite temperature $2k_1 \simeq k_2$, considering the statistical factor, the α value will tend to 1.

TABLE 3—MEAN VALUES OF 1000 lnα FOR ALKALINE EARTH CARBONATES AT DIFFERENT TEMPERATURES.

Temperature	25°C	30°C	36°C	45°C	55°C	62°C
Mean 1000 lnα for $CaCO_3$	7.99	7.86	7.69	7.42	7.17	7.00
Mean 1000 lnα for $SrCO_3$	8 20	8 09	7.92	7.63	7.36	7.18
Mean 1000 lnα for $BaCO_3$	8 65	8.50	8.35	8.12	7.86	7.68

Further, it is clear that αHBr decreases with temperature. On plotting 1000 ln α against $\frac{1}{T}$ a straight line is obtained, suggesting an empirical relationship, $1000 \ln \alpha = \frac{A}{T} + B$, between fractionation factor α and temperature T. The values for A are 2.67×10^3, 2.90×10^3 and 2.55×10^3 and that for B are −0.97, −1.48, and 0.09 for $CaCO_3$, $SrCO_3$ and $BaCO_3$ respectively.

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Synthesis of Some Sulfonamide Derivatives

M. S. SHINGARE and D. B. INGLE*

Chemistry Department, Marathwada University, Aurangabad-431 002.

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Various 2-(sulfamyl substituted anilino)-4-(substituted phenyl) thiazoles were prepared by the condensation of different 2-chloroacetophenones with few sulfamyl substituted phenyl thioureas. The presence of imino (-NH-) and -SO_2NH_2 groups were confirmed by IR spectra. Some of the type compounds were tested against antibacterial activity and found to be ineffective.

THE antihistaminic and antianaleptic properties of some secondary and tertiary thiazolyl amines[1], the fungicidal activity of some 2-anilino thiazoles[2] and the antimalerial activity of some anilino thiazoles[3] have been reported. The present paper deals with the synthesis of 2-(sulfamyl substituted anilino)-4-(substituted phenyl) thiazoles with view to ascertaining their possible antibacterial activity. They were obtained by the condensation of different substituted 2-chloro-acetophenones with sulfamyl substituted phenyl thioureas which incidentally have so far not been reported in the literature. The procedure described by Frank and Smith[4] was adopted for the preparation of sulfamyl phenyl thioureas which were used as intermediates for the synthesis of 2-anilino thiazole compounds.

The different 2-chloro acetophenones, *viz.* 2-chloro-, 2,4'-dichloro-, 2-chloro-4'-methyl-, 2-chloro-4'-bromo-, 2-chloro-4'-iodo-, 2-chloro-2'-fluoro-5'-methyl-, were prepared by Friedel-Craft method and were condensed with thiourea. The melting points of 2-amino-4-(substituted phenyl) thiazoles so obtained corresponded with literature values[5-7]. Similarly melting points of 2,2',5'-trichloro-, 2,3',4'-trichloro-, 2,2'-dichloro-6'-methyl-, 2-chloro-2'-bromo-5'-methyl acetophenones agreed with reported values[8].

Experimental

1. *Synthesis of sulfamyl phenyl thiourea :*

A mixture of ammonium thiocyanate (8g., 0.11 mol.) and acetone (50 ml) was placed in the flask. Benzoyl chloride (15g., 0.1 mol) was added through the dropping funnel with stirring. Sulfonamide (17g., 0.1 mol) in acetone (50 ml) was then added in small portions. When the addition was over, the reaction mixture was refluxed for 30 min and cooled. It was poured over 500 ml ice-cooled water. The precipitate was separated by filtration. The precipitate was heated for half an hour with 10% NaOH solution (100 ml) and cooled. The clear solution was neutralised by dil HCl. The precipitate obtained was filtered and washed with 2% $NaHCO_3$ solution. Compound was recrystallised from ethanol. M.p. 206°. Yield 20g. (85%). The melting point was in agreement with that reported by James Walker[9] ;

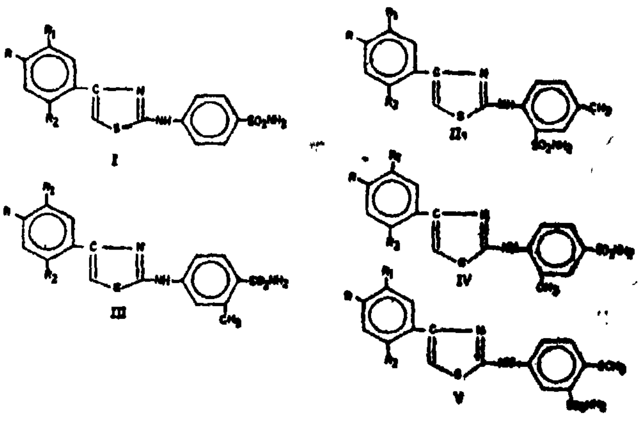


Fig : (I) to (V) :

$R=H$, $R_1=H$, $R_2=H$.
$R=Me$; $R_1=H$, $R_2=H$.
$R=Cl$, $R_1=H$, $R_2=H$.
$R=Br$, $R_1=H$, $R_2=H$.
$R=I$, $R_1=H$, $R_2=H$.
$R=Cl$, $R_1=Cl$, $R_2=H$.
$R=H$, $R_1=Cl$, $R_2=Cl$.
$R=H$, $R_1=Me$, $R_2=Cl$.
$R=H$, $R_1=Me$, $R_2=Br$.
$R=H$, $R_1=Me$, $R_2=F$.

Similarly the other 2-sulfamyl-4-methyl-, 4-sulfamyl-3-methyl-, 4-sulfamyl-2-methyl-, 3-sulfamyl-4-methoxy-phenylthioureas were prepared from respective amines : 2-amino-5-methyl-, 4-methyl-6-amino-, 3-methyl-4-amino-, 3-amino-6-methoxy benzene sulfonamides. The melting points, percentage yields and elemental analysis are given in Table 1.

* For correspondence.

TABLE 1—SULFAMYL SUBSTITUTED PHENYL THIOUREAS.

Phenyl thiourea	M.P. °C	Yield %	Elemental analysis Calcd C%	H%	Found C%	H%
4-sulfamyl	206	85	36.36	3.89	36.51	4.10
2-sulfamyl-4-methyl	205	75	39.18	4.48	39.26	4.67
3-methyl-4-sulfamyl	220	85	39.18	4.48	39.26	4.58
2-methyl-4-sulfamyl	193	76	39.18	4.48	39.40	4.52
3-sulfamyl-4-methoxy	213	50	36.78	4.21	36.93	4.34

The sulfamyl substituted phenylthiourea showed absorption due to -NH group. The NH asymmetric stretching frequencies of these compounds lie in the range of 3200-3450 cm^{-1} with higher intensity. The -NH symmetric stretching frequencies show in the range of 3080-3200 cm^{-1}. The $-SO_2NH_2$ group showed absorption in the range of 1335 to 1370 cm^{-1} and 1145 to 1180 cm^{-1} due to asymmetric and symmetric stretching vibration of S=O respectively.

2. *General procedure for the synthesis of (2-sulfamyl substituted anilino)-4-(substituted phenyl) thiazoles.*

Sulfamyl substituted phenyl thiourea (0.01 mol) was dissolved in hot water and treated with (0.01 mol) of 2-chloro acetophenones in the presence of alcohol. The reaction mixture was left on the water bath for 2 hr. On cooling a solid separated. The remainder of the product was precipitated as micro-crystalline solid by the addition of an excess of sodium bicarbonate solution. All the compounds were recrystallised from alcohol.

By following above procedure other sulfamyl substituted phenyl thioureas were condensed with differently substituted 2-chloro acetophenoes. The melting points, percentage yields and elemental analysis are given in the Tables 2 to 6.

TABLE 2—2-(4′-SULFAMYL ANILINO)-4-(SUBSTITUTED PHENYL) THIAZOLES : (I)

Phenyl substituent at-4-position	M.P. °C	Yield %	Elemental analysis Calcd C%	H%	Found C%	H%
R, R_1, R_2 = H	240	75	54.39	3.93	54.65	4.21
R = Me, R_1, R_2 = H	251*	78	55.65	4.35	55.68	4.45
R = Cl, R_1, R_2 = H	240	78	49.25	3 28	50.05	3.85
R = Br, R_1, R_2 = H	255	76	43.90	2.92	43.87	2.90
R = I, R_1, R_2 = H	226	81	39.40	3.85	40.05	2.63
R, R_1 = Cl, R_2 = H	230	87	44.88	2.99	45.21	3.25
R = H, R_1, R_2 = Cl	199	87	44.88	2.99	45.20	3.15
R = H, R_1, Me, R_2 = Cl	177	90	55.81	4.07	56.01	4.25
R = H, R_1 = Me, R_2 = Br	167	85	46.57	3.65	46.31	3.46
R = H, R_1 = Me, R_2 - F	226	80	52.89	3.85	52.98	3.65

* Crystallised from AcOH.

TABLE 3—2-(2′-SULFAMYL-4′-METHYL ANILINO)-4-(SUBSTITUTED PHENYL) THIAZOLES : (II)

Phenyl Substituent at-4-position	M.P. °C	Yield %	Elemental analysis Calcd C%	H%	Found C%	H%
R, R_1, R_2 = H	213	78	55.65	4.34	55.72	4.56
R = Me, R_1, R_2 = H	238*	80	56.82	4.73	56.90	4.89
R = Cl, R_1, R_2 = H	240	80	50.59	3.68	50.73	3.86
R = Br, R_1, R_2 = H	265	76	45.28	3.30	45.18	3.43
R = I, R_1, R_2 = H	257*	74	40.76	2.97	40.86	3.03
R, R_1 = Cl, R_2 = H	236	80	46.37	3.14	46.80	3.39
R = H, R_1, R_2 = Cl	190	80	46.37	3.14	46.80	3.39
R = H, R_1 = Me, R_2 = Cl	194	81	51.84	4.07	56.01	4.25
R = H, R_1 = Me, R_2 = Br	177	84	46.57	3.65	46.83	3.76
R = H, R_1 = Me, R_2 = F	216	80	54.11	4.24	54.50	4.40

TABLE 4—2-(3′-METHYL-4′-SULFAMYL ANILINO)-4-(SUBSTITUTED PHENYL) THIAZOLES : (III)

Phenyl Substitutent at-4-position	M.P. °C	Yield %	Elemental analysis			
			Calcd		Found	
			C%	H%	C%	H%
$R=H,R_1,R_2=H$	180	76	55.65	4.34	55.71	4.39
$R=Me,R_1,R_2=H$	164	80	56.82	4.73	56.93	4.87
$R=Cl,R_1,R_2=H$	150	76	50.59	3.68	50.65	3.76
$R=Br,R_1,R_2=H$	215	85	45.28	3.30	45.51	3.67
$R=I,R_1,R_2=H$	145	75	40.76	2.97	40.89	3.26
$R=R_1=Cl,R_2=H$	249	84	46.37	3.14	46.54	3.54
$R=H,R_1,R_2=Cl$	207	85	46.37	3.14	46.30	3.43
$R=H,R_1=Me,R_2=Cl$	215	90	51.84	4.07	51.86	4.10
$R=H,R_1=Me,R_2=Br$	204	85	46.57	3.65	46.42	3.85
$R=H,R_1=Me,R_2=F$	173	80	54.11	4.24	54.31	4.30

TABLE 5—2-(2′-METHYL-4′-SULFAMYL ANILINO)-4-(SUBSTITUTED PHENYL) THIAZOLES : (IV)

Phenyl substituent at-4-position	M.P. °C	Yield %	Elemental analysis			
			Calcd		Found	
			C%	H%	C%	H%
$R,R_1,R_2=H$	196	80	55.65	4.34	55.90	4.70
$R=Me,R_1,R_2=H$	225	76	56.82	4.73	56.89	4.48
$R=Cl,R_1,R_2=H$	245	78	50.59	3.68	50.29	3.72
$R=Br,R_1,R_2=H$	235	81	45.28	3.30	45.43	3.09
$R=I,R_1,R_2=H$	195	75	40.76	2.97	40.74	2.92
$R,R_1=Cl,R_2=H$	248	85	46.37	3.14	46.50	3.36
$R=H,R_1,R_2=Cl$	237	84	46.37	3.14	46.61	3.43
$R=H,R_1=Me,R_2=Cl$	202	85	51.84	4.07	51.86	4.10
$R=H,R_1=Me,R_2=Cl$	174	85	46.57	3.65	46.50	3.40
$R=H,R_1=Me,R_2=F$	157	80	54.11	4.24	54.41	4.37

TABLE 6—2-(3′-SULFAMYL-4′-METHOXY ANILINO)-4-(SUBSTITUTED PHENYL) THIAZOLES : (V)

Phenyl substituent at-4-position	M.P. °C	Yield %	Elemental analysis			
			Calcd		Found	
			C%	H%	C%	H%
$R,R_1,R_2=H$	233	85	53.18	4.15	53.26	4.34
$R=Me,R_1,R_2=H$	242*	85	54.40	4.53	54.71	4.69
$R=Cl,R_1,R_2=H$	254	81	48.54	3.53	48.59	3.76
$R=Br,R_1,R_2=H$	267	76	43.63	3.18	43.49	3.48
$R=I,R_1,R_2=H$	238	73	39.42	2.87	39.72	3.10
$R,R_1=Cl,R_2=H$	252*	80	44.65	3.02	44.80	3.37
$R=H,R_1,R_2=Cl$	240	80	44.65	3.02	44.76	3.41
$R=H,R_1=Me,R_2=Cl$	194	85	49.81	3.90	45.06	4.12
$R=H,R_1=Me,R_2=Br$	187	85	44.83	3.73	45.24	4.12
$R=H,R_1=Me,R_2=F$	225*	80	51.90	4.07	52.33	4.42

*Crystallised from AcOH.

The IR spectra showed absorption due to imino (-NH-) group and (-SO_2NH_2) group and due to thiazole nucleus : The -NH stretching frequencies of these compounds lie in the range of 3320 to 3500 cm^{-1} with higher intensity. The -NH bending frequencies show absorption in the range of 1600 to 1640 cm^{-1}. All the compounds show absorption due to asymmetric stretching of S=O (1370, 1330 cm^{-1}) and symmetric stretching of S=O (1180, 1160cm^{-1}) groups. The absorption due to thiazole nucleus showed band around 1570, 1440, 1365, 1020, 815 cm^{-1}.

Activity : The 2-(sulfamyl substitutedanilino)-4-(substituted phenyl) thiazoles, selecting few of compounds from each series were tested for the antibacterial activity, against *Staphylococcus aureus*, *S. typhi*, and *S. comma* and found to be inactive.

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Synthesis of 5-Hydroxy-1,2-Diphenylindole Derivatives

G. S. GADAGINAMATH, L. D. BASANAGOUDAR and S. SIDDAPPA*

Department of Chemistry, Karnatak University, Dharwar-580003.

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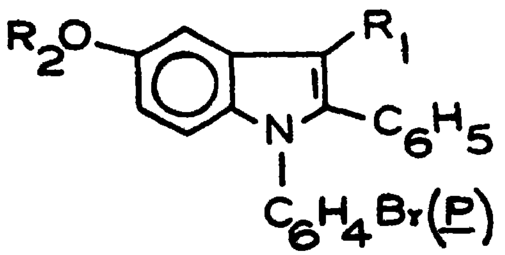
1-*p*-Bromophenyl-5-benzyloxy-2-phenylindole was synthesised by the Nenitzescu method and converted to various N-substituted 1-*p*-bromophenyl-5-benzyloxy-2-phenyltryptamines. Attempts to debenzylate the above tryptamines by hydrogenation with Pd/C gave the corresponding 5-hydroxy-1,2-diphenyl-N-substituted tryptamines resulting from debromination during the process. Similar debromination with ethyl 1-*p*-bromophenyl-5-hydroxy-2-phenylindole-3-carboxylate and its 4-dimethylamino derivative is reported.

IN continuation of our previous work on the synthesis of indole derivatives of biological interest,[1-4] we report here the synthesis of some 5-hydroxy-1, 2-diphenyl indole derivatives. Ethyl β-*p*-bromoanilinocinnamate (1) was reacted with *p*-benzoquinone to get ethyl 1-*p*-bromophenyl-5-hydroxy-2-phenylindole-3-carboxylate (2) which was benzylated to yield 5-benzyloxyindolecarboxylate (3). This was converted to the acid (4) which decarboxylated to yield 1-*p*-bromophenyl-5-benzyloxy-2-phenylindole (5). The indole (5) was reacted[5] with oxalyl chloride to get 3-indolylglyoxyl chloride which on subsequent treatment with pyrrolidine and cyclohexylamine gave the corresponding amides (6 & 7). Reduction of these amides (6 & 7) with LAH provided the required 1-*p*-bromophenyl-5-benzyloxy-2-phenyltryptamines (8 & 9) which were hydrogenated over Pd/C (10%) with a view to obtain the free 5-hydroxy analogues. During debenzylation, debromination also occurred to yield 5-hydroxy-1,

Scheme 1

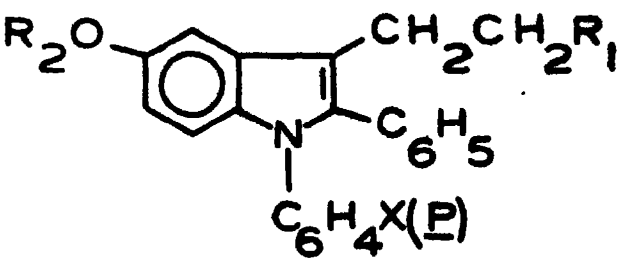
$C_6H_5-C(=CH-COOC_2H_5)-NH-C_6H_4Br(P)$

(1)



(2 — 7)

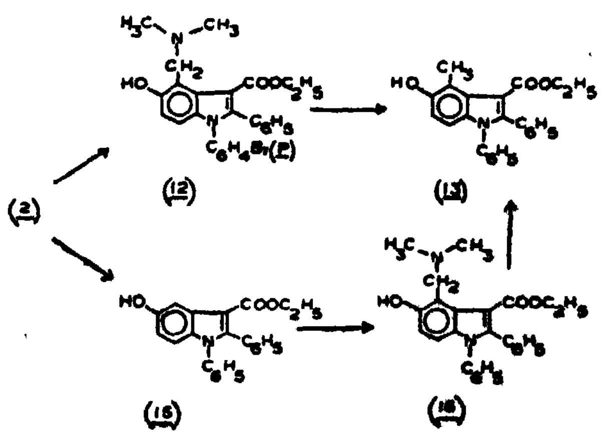
R₁	R₂
(2) $-COOC_2H_5$	$-H$
(3) $-COOC_2H_5$	$-CH_2C_6H_5$
(4) $-COOH$	$-CH_2C_6H_5$
(5) $-H$	$-CH_2C_6H_5$
(6) Pyrrolidinoglyoxyl	$-CH_2C_6H_5$
(7) Cyclohexylamidoglyoxyl	$-CH_2C_6H_5$



(8 — 11)

	R_1	R_2	X
(8)	Pyrrolidino	$-CH_2C_6H_5$	Br
(9)	Cyclohexylamino	$-CH_2C_6H_5$	Br
(10)	Pyrrolidino	$-H$	$-H$
(11)	Cyclohexylamino	$-H$	$-H$

Scheme 2



* 13, Basappa Layout, Gavipuram, Bangalore-560019.

2-diphenyltryptamines (10 & 11). The C-Br stretching band (around 520s cm^{-1}) observed in the IR spectra of bromo compounds (8 & 9) is not present in the spectra of debrominated products (10 & 11).

Similarly, when the 4-*iso*gramine (12) was treated with Raney Ni in refluxing ethanol, the elimination of bromine took place and ethyl 4-methyl-5-hydroxy-1, 2-dipenylindole-3-carboxylate (13) was obtained. The IR spectrum of (12) shows C-Br stretching band at 515s cm^{-1}, which is absent in the I. R. spectrum of (13). The PMR results of (12) and (13) agree with their structures. Aromatic region (6.6 - 7.66 δ) of (12) accounts for eleven protons while that of (13) (6.76 - 7.66 δ) for twelve protons. The C-6 proton signal of (12) is observed as doublet (J = 9 Hz) at 6.71 and the J value indicates *ortho*-coupling. This confirms the presence of dimethylaminomethyl group [4.13 δ ($-CH_2$) ; 2.45 δ two methyls] at C-4. Further, compound (13) has been synthesised by an unambiguous method from 4-*iso*gramine (16) *via* (15).

The elimination of halogen bound to aromatic compounds has been reported[a] during hydrogenation using Pd/C (10%) or Reney Ni and the alkaline medium has been noted[aa] to accelerate the elimination process. During the debenzylation of 5-benzyloxytryptamines (8 & 9) and the conversion of 4-*iso*gramine (12) to 4-methylindole derivative (13), the reaction medium is basic due to the basic nitrogen present in the starting compounds (8, 9 & 12). Further, when ethyl 1-*p*-bromophenyl-5-hydroxy-2-phenylindole-3-carboxylate(2), which does not contain any basic nitrogen was hydrogenated over Pd/C (10%) or Raney Ni or refluxed with Raney Ni in ethanol the bromine was eliminated yielding ethyl 5-hydroxy-1, 2, diphenylindole-3-carboxylate (15) whose structure was confirmed by an unambiguous synthesis from ethyl β-anilinocinnamate (14) and *p*-benzoquinone. The above results appear to indicate the labile nature of the bromine situated at the *para* position of the phenyl group attached to indole nitrogen.

Experimental

Ethyl β-p-bromoanilinocinnamate (1)

A mixture of ethyl benzoylacetate (35 g), *p*-bromoaniline (35 g) and concentrated hydrochloric acid (5 drops) was heated at 65-70° for 16 hr. It was cooled and the product was recrystallised from alcohol as yellow flakes (30 g), m. p. 114°.

(Found : C, 58.72 ; H, 4.84 ; N, 4.21. $C_{17}H_{18}No_2Br$ requires C, 58.95 : H, 4.62 ; N, 4.05%).

Ethyl 1-p-bromophenyl-5-hydroxy-2-phenylindole-3-carboxylate (2)

A solution of cinnamate (1) (34 g) and *p*-benzoquinone (21 g) in ethanol was refluxed for 16 hr and the residue obtained on removing ethanol under suction was purified by crystallisation from benzene. The product on recrystallisation from ethyl acetate gave colourless tiny needles (8 g), m. p. 250°.

(Found : C, 63.13 ; H, 4.07 ; N, 3.36. $C_{23}H_{18}NO_3Br$ requires C, 63.30 ; H, 4.23 ; N, 3.21%) ; ν_{max}^{nujol} cm^{-1} 3290br (OH) ; 1648s (C=O) and 505s C-Br).

Ethyl 1-p-bromophenyl-5-benzyloxy-2-phenylindole-3-carboxylate (3)

Benzyl chloride (1.8 ml) was added to a solution of hydroxyindole (2) (6 g) and sodium hydroxide (1.8 g) in a mixture of water (12 ml) and alcohol (36 ml). The mixture was heated under reflux on a water bath until crystalline benzyloxyindole (3) separated (10-15 min). The benzyloxyindole was collected and was recrystalised from benzene-petroleum ether (60-80°) as colourless plates (2 g), m. p. 203°.

(Found : C, 68.71 ; H, 4.69 ; N, 2.78. $C_{30}H_{24}NO_3Br$ requires C, 68.60 ; H, 4.56 ; N, 2.66%).

1-p-Bromophenyl-5-benzyloxy-2-phenylindole-3-carboxylic acid (4)

The carboxylate (3) (1.9 g) in benzene (20 ml) was hydrolysed with alcoholic potassium hydroxide solution (25%, 30 ml) by heating under reflux for 5 hr. The potassium salt of the acid (4) obtained on evaporating the solvents was suspended in ice water (100 ml) and acidified with acetic acid. The precipitate was collected and recrystallised from aqueous dioxan as colourless granules (1.5 g), m. p. 254°.

(Found : C, 67.40 ; H, 4.30 ; N, 2.96. $C_{28}H_{20}NO_3Br$ requires C, 67.47 ; H, 4.02 ; N, 2.81%).

1-p-Bromophenyl-5-benzyloxy-2-phenylindole (5)

The acid (4) (3 g) was heated at 255-258° for 20 min. (i.e. until the evolution of CO_2 ceased) and the residue was recrystallised from benzene-petroleum ether (60-80°) to get the *benzyloxyindole* (5) as colourless needles (1.8 g), m.p. 157°.

(Found : C, 71.54 ; H, 4.57 ; N, 3.17. $C_{27}H_{20}NOBr$ requires C, 71.36 ; H, 4.40 ; N, 3.08%).

1-p-Bromophenyl-5-benzyloxy-2-phenyl-3-(2-N-pyrrolidinoglyoxyl) indole (6)

The benzyloxyindole (5) (2 g) in dry ether (300 ml) was treated with oxalyl chloride (2.8 ml) according to the procedure described earlier[5] and the greenish yellow tiny needles of *3-indolylglyoxyl chloride* was collected (1.9 g), m.p. 138-139° ; ν_{max}^{Nujol} cm^{-1} absent (OH) ; 1640s (conjugated C=O) ; 1795s (COCl). This indolylglyoxyl chloride (1.8) was treated with pyrrolidine

(4 ml) and the separated amide (6) was recrystallised from aqueous dioxan as colourless needles (1.7 g), m.p. 194°.

(Found : C, 68.18 ; H, 4.75 ; N, 4.96. $C_{33}H_{27}N_2O_3Br$ requires C, 68.39 ; H, 4.66 ; N, 4.84%) ν_{max}^{Nujol} cm^{-1} 1628s (C=O) ; absent (OH).

1-p-Bromophenyl-5-benzyloxy-2-phenyl-3-(2-N-cyclohexylamidoglyoxyl) indole (7)

Following the procedure described for (6), the amide (7) was prepared from indole (5) (2 g), oxalyl chloride (2.8 ml) and cyclohexyl amine (4 ml). It was recrystallised from aqueous dioxan as colourless tiny needles (1.8 g), m.p. 216°.

(Found : C, 69.04 ; H, 5.21 ; N, 4.78. $C_{35}H_{31}N_2O_3Br$ requires C, 69.18 ; H, 5.11 ; N, 4.61%).

1-p-Bromophenyl-5-benzyloxy-2-phenyl-3-(2-N-pyrrolidinoethyl) indole (8)

A solution of the amide (6) (1.6 g) in dry tetrahydrofuran (100 ml) was added to a suspension of lithium aluminium hydride (2.5 g) in dry ether (100 ml) and the mixture was heated under reflux for 24 hr. It was cooled, the complex was decomposed with sodium hydroxide solution (15%, 2.5 ml) and water (5 ml). The white precipitate was filtered off and the residue obtained on evaporating solvents was crystallised from alcohol as colourless plates (1 g), m.p. 128°.

(Found : C, 71.93 ; H, 5.46 ; N, 5.21 ; $C_{33}H_{31}N_2OBr$ requires C, 71.86 ; H, 5.63 ; N, 5.08%) ν_{max}^{Nujol} cm^{-1} absent (OH & C=O) ; 1618w and 1595m (Ar C=C) ; 520s (C-Br).

1-p-Bromaphenyl-5-benzyloxy 2-phenyl 3-(2-N-cyclohexylaminoethyl) indole (9)

The tryptamine (9) was prepared from amide (7) (2 g) and lithium aluminium hydride (3 g) according to the procedure given for (8) and the product was recrystallised from benzene-petroleum ether (60-80°) as colourless plates (1.2 g), m.p. 170°.

(Found : C, 72.63 ; H, 5.91 ; N, 4.88. $C_{35}H_{35}N_2OBr$ requires C, 72.52 ; H, 6.05 ; N, 4.84%) ν_{max}^{Nujol} cm^{-1} absent (C=O) ; 3290s (NH) and 520s (C-Br).

1, 2-Diphenyl-5-hydroxy-3-(2-N-pyrrolidinoethyl)-indole (10)

A mixture of benzyloxytryptamine (8) (0.5 g) and palladium charcoal (10%, 0.45 g) in methanol was hydrogenated in a Parr low pressure apparatus at 53- 5 lb/sq. inch. for 10-12 hr. The catalyst was filtered off and the residue obtained from the filtrate on removing methanol under suction, was recrystallised from methanol as pale yellow microscopic needles (0.2 g), m.p. 205°.

(Found : C, 81.46 ; H, 6.93 ; N, 7.41. $C_{26}H_{26}N_2O$ requires C, 81.68 ; H, 6.81 ; N, 7.33%) ν_{max}^{Nujol} cm^{-1} 3430br (OH) ; 1608 and 1560w (Ar C=C) ; absent (C-Br).

1, 2-Diphenyl-5-hydroxy-3-(2-N-cyclohexylaminoethyl) indole (11)

Following the procedure described for (10), the benzyloxytryptamine (9) (0. g) was hydrogenated over Pd/C (10% 0.45 g) and the product was crystallised from benzene-petroleum ether as pale yellow granules (0.2 g), m.p. 218°(d).

(Found : C, 82.01 ; H, 7.13 ; N, 6.65. $C_{28}H_{30}N_2O$ requires C, 81.94 ; H, 7.32 ; N, 6.83%) ν_{max}^{Nujol} cm^{-1} 3340br (NH/OH) ; 1605s and 1560m (Ar C=C) ; absent (C-Br).

Ethyl 1-p-bromophenyl-4-dimethylaminomethyl-5-hydroxy-2-phenylindole-3-carboxylate (12)

The hydroxyindole (2) (4 g) in dioxan (20 ml) was subjected to the Mannich reaction with dimethylamine (30%, 3 ml), formaldehyde (37%, 1 ml) and acetic acid (8 ml) according to the procedure described earlier[4] and the *4-isogramine* (12) obtained was crystallised from aqueous alcohol as colourless plates (3 g), m.p. 183°.

(Found : C, 63.·6 ; H, 4.91 ; N, 5.54. $C_{26}H_{25}N_2O_3Br$ requires C, 63.30 ; H, 5.07 ; N, 5 68%) ν_{max}^{Nujol} cm^{-1} 515s (C-Br) ; PMR, $CDCl_3$ (TMS), δ ppm 0.88 (3H, t, J=7Hz ester CH_3) ; 4.03 (2H, q, ester -CH_2), 2.45 (6H, s, N(CH_3)$_2$) ; 4.13 (2H, s, N-CH_2) ; 6.71 (1H, d, J=9Hz, C-6H) ; 10.88 (1H, br, C-5 OH) ; 6.6-7.66 (11H, m, ArH).

Ethyl 4-methyl-5-hydroxy-1, 2-diphenylindole-3-carboxylate (13)

Method A

A mixture of 4-*iso*gramine (12) (3 g) and Raney nickel (30 g) in ethanol (300 ml) was heated under reflux for 24 hr and then filtered. The residue obtained on evaporating ethanol under suction was crystallised from ethanol to get the pure carboxylate (13) as colourless plates (2 g), m.p. 167°.

(Found : C, 77.79 ; H, 4 35 ; N, 3.85. $C_{24}H_{21}NO_3$ requires C,77.62 ; H,4.49 ; N,3.77%) ; TLC [Silica gel G, benzene-ethyl acetate (6 : 1)] Rf 0.62 ; ν_{max}^{Nujol} cm^{-1} 3405s (OH) ; 1653 (C=O) and absent (C-Br) ; PMR, DMSO-d_6 (TMS) δppm 0.95 (3H, t J=7Hz, ester CH_3) ; 4.1 (2H, q, ester-CH_2-) ; 3.46 (3H, s, C-4 CH_3) ; 8.96 (1H, s, C-5 OH) ; 6.76-7.66 (12H, m, ArH).

Method B

Following the procedure described in method A, a mixture of 4-*iso*gramine (16) (0.3 g) and Raney nickel (3 g) in ethanol (30 ml) was refluxed and the product was crystallised from alcohol as colourless

plates (0.25 g), m.p. 167°. This showed no depression in mixed m.p. with (13) and exhibited identical TLC behaviour with (13).

Ethyl β-anilinocinnamate (14)

Ethyl benzoylacetate (30 g) was reacted with aniline (20 g) according to the procedure given for (1) and the product was crystallised from alcohol to get (14) as pale yellow plates (25 g), m.p. 65°.

(Found : C, 76.29 ; H, 6.48 ; N, 5.36. $C_{17}H_{17}NO_2$ requires C, 76,40 ; H 6.37 ; N, 5.24%).

Ethyl 5-hydroxy-1, 2-diphenylindole-3-carboxylate (15)

Method A

A solution of the cinnamate (14) (10 g) and benzoquinone (7 g) in alcohol (100 ml) and acetic acid (5 ml) was heated under reflux for 16 hr and the residue obtained on removing solvent under suction was purified from benzene and then repeatedly crystallised from ethyl acetate to get pure carboxylate (15) as colourless plates (2 g), m.p. 264° ; TLC [Silica gel G, benzene-ethyl acetate (7 : 1)] Rf 0.54.

(Found : C, 77.46 : H, 5.21 ; N, 4.03. $C_{23}H_{19}NO_3$ requires C, 77.31 ; H, 5.32 ; N, 3.92%).

Method B : Hydrogenation of bromo compound (2) with Pd/C catalyst

A mixture of bromo compound (2) (0.2 g) and Pd/C (10%, 0.2 g) in methanol (100 ml) was hydrogenated according to the procedure described for (10) and the product was recrystallised from ethyl acetate to get (15) as colourless plates (0.1 g), m.p. 264°. No depression in mixed m.p. with sample (15) synthesised according to method A and showed identical TLC behaviour.

Method C : Hydrogenation of bromo compound (2) with Raney Nickel catalyst

The bromocompound (2) (0.3 g) in methanol (150ml) was hydrogenated over Raney Ni as described in Method B and the product on crystallisation from ethyl acetate was obtained as colourless plates (0.12 g), m.p. 264°. No depression in mixed m.p. with synthetic sample (15) (Cf. Method A) and showed identical TLC behaviour.

Method D

The bromocompound (2 (0.2 g) in ethanol (20 ml) was treated with Raney nickel (6 g) as described for (13) (Method A) and the product was crystallised from ethyl acetate as colourless plates (0.16 g), m.p. 264°. No depression in mixed m.p. with synthetic sample (15) and showed identical TLC behaviour.

Ethyl 4-dimethylaminomethyl-5-hydroxy-1, 2-diphenylindole-3-carboxylate (16)

Following the procedure described for (12), the *4-isogramine* (16) was prepared from the corresponding hydroxyindole (15) (0.6 g), dimethylamine (0.6 ml) and formaldehyde (0.2 ml) and crystallised from aqueous methanol as colourless tiny needles (0.45 g), m.p. 184°.

(Found : C, 75.48 ; H, 6.12 ; N, 6.87. $C_{26}H_{26}N_2O_3$ requires C, 75.37 ; H, 6.28 ; N, 6.76%).

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Comparative Study of the Eutectic Bodied Oil with Stand Oil

S. N. KOLEY* and A. E. RHEINECK

Department of Polymers and coatings, North Dakota State University, Fargo, N. D. 58102, U.S.A.

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The eutectic bodied oil was compared with thermally bodied oil like stand oil. The methyl esters of the stand oil were separated into different fractions by distillation, urea—adductation and by column chromatography. All the fractions were analyzed by physical and chemical methods and by IR & NMR spectroscopies. Unlike the eutectic bodied oils, stand oil is free from any aromatic or other compounds. The diallylic protons appear to be most reactive in all the cases, however, these protons are more reactive in the preparation of eutectic bodied oils. In case of stand oil, Diels-Alder reaction is more prominent.

IN the previous papers[1,2] attempts were made to find out the composition of the oils bodied by eutectic saltmixtures. To compare the eutectic bodied oils, with thermally bodied oils, stand oils were also analyzed. The thermal dimerization product of methyl-*trans*-10-*trans*-12-octadecadienoate obtained by heating at 250° was investigated[3]. The dimer structure was shown to be a Diels-Alder reaction product. Polymerization by Diels-Alder reaction takes place in two different ways namely, (1) intermolecularly, (2) intra-molecularly. Besides the occurrence of these inter-and intra-molecular reactions during polymerization, there is cyclization of single fatty acid molecule containing two or more double bonds with the consequence that cyclohexene rings are formed. The excessive loss of unsaturation without consequent rise in viscosity has been attributed to cyclization changes in fatty acids. It has also been suggested that the initial sharp decrease in iodine value while cooking oils to produce stand oil is likely to be due to the cyclization of dienoic and trienoic acid radicals present in the oil, in the early stages of production[4].

Now it is to be decided whether Diels-Alder reaction is the main or sole reaction of polymerization. To answer this point the dimers were produced by heat treatment of a variety of materials such as methyl-L-eleostearate, methyl linoleate, methyl linolenate and sunflower oil. By suitably directed degradations of these dimers it was established that six membered rings were in fact present. The dimers were brominated and oxidized by potassium permanganate to convert the substituted cyclohexenes to tetracarboxylic acids. The yield of the tetracarboxylic acids was of a few percentage which makes it doubtful that it is the sole reaction in oil polymerization. It may be possible that other type of reaction is taking place. This probability has recently received strong support from kinetic studies on the polymerization of methyl 9, 12-linoleate[5].

These studies showed that a prior isomerization occurs, but it was shown that at least 80% of the dimer was formed by reaction mechanism not involving conjugated molecules. The initial stages in the direct dimerization reaction is postulated on kinetic evidence to be a disproportionation reaction or in other words a hydrogen atom presumably from the 11-methylene group in one molecule is transferred to another molecule resulting in the formation of two free radicals. If the lone electron form in one radical pairs with the lone electron of the other, a dimer with C-C linkage will be formed[5].

Intermolecular addition polymerization is not the only reaction through which glyceride can dimerize. Glyceride dimers may also be formed through interesterification reaction between glyceride monomers that contain dimeric fatty acid group as a result of intermolecular addition. It is shown that a considerable part of the overall molecular weight increases are due to this interesterification mechanism.

The most desirable configuration about the unsaturated linkages during the diene reaction is the *trans, trans* conjugated configuration. The *cis, trans* form is less suitable and *cis, cis* form is unsuitable. These facts can be reasonably deduced from the inspection of Fischer-Hirschfelder-Taylor models of such molecules which made it apparent that in the first case there is no interference to rotation around the central bond, whereas in the last case there is considerable steric hindrance[6].

Experimental

The method of preparation of eutectic bodied oils and the apparatus used in the preparation are described in the previous paper ([1]). The methods of analyses and experimental techniques are also described in the previous papers[1,2]. Three different samples of stand oil from linseed oil having different viscosities were prepared by heating at 300° under nitrogen atmosphere as shown in Table 1. The stand oils were fractionated in two different fractions, namely acetone-soluble and insoluble fractions using 2 volumes of dry acetone at 25°. The methyl esters of the stand oils, the acetone soluble and insoluble fractions were prepared by

* For correspondence—Directorate of Industries, Industrial Research Laboratory, Canal South Road, Calcutta-15.

TABLE 1—PREPARATION OF STAND OILS & EUTECTIC BODIED OILS.

Sample No.	Type of Bodied Oil	Viscosity (Stokes)
18	Stand	1.21
19	Stand	4-4.36
20	Stand	17.56
21	Eutectic	1.21
22	Eutectic	4-4.36

TABLE 2—INFRA-RED DATA OF METHYL ESTERS OF ORIGINAL LINSEED OIL AND STAND OIL FRACTIONS.

Frequency (Cm^{-1})	Assignment	Linseed Oil	18 S	18 I
3410-3510	-OOH/-OH			
3010	*cis* -CH=CH			
2920	C-H Stretching			
2850	,,			
1740	C-O Stretching of Ester			
1550	Phenyl nucleus	a	a	
965	Isolated trans	a	a	

<table>
<tr><th>19 S</th><th>19 I</th><th colspan="2">20</th><th colspan="2">21</th><th colspan="2">22 S</th><th colspan="2">22 I</th></tr>
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Dist=Distillate, Res=Residue, tr=trace, a=absent, Blank spaces indicate present.

analyzed in Varian A60A Model NMR spectrophotometer and the summary of the results are given in Table 3. The methyl esters of the stand oils were fractionated in two fractions, namely, urea-adductable and-nonadductable fractions. These fractions were also analyzed by NMR and the summary of the results are shown in Table 4. The methyl esters of bodied oils were also separated by column chromatographic technique into three fractions, namely, monomer, dimer and polymer. The monomer and dimer fractions were analyzed by NMR and the summary of the results are shown in Table 5. It was not possible to analyze the polymer fractions due to paucity of the samples.

Discussions

The results show that oxygenated groups like -OH/-OOH are present only in residue fractions of acetone-soluble and insoluble fractions (Table 2). All the fractions, however, are enriched with *trans* isomers. Table 3 shows that the formation of cyclohexene protons is higher in the stand oil than the eutectic bodied oils. Table 3 shows the analyses of eutectic bodied oils and stand oils. The olefinic protons have been decreased to 2.1 in the residue from insoluble fractions of sample 22, which is called 22 I (res). Unlike the eutectic bodied oils all the fractions of stand oils are free from any aromatic compounds. The decrease in diallylic protons is remarkable in all the cases. In sample 20, the diallylic protons have been decreased to 1.9 (3.0 in the original) while the olefinic protons have been decreased to only 3.8. In case of the eutectic bodied oils, the diallylic protons have been decreased to 1.5. The number of olefinic protons in 22S is very slightly higher than that of 22I indicating thereby that unsaturated double bonds are not the major reacting centers. The diallylic protons have been decreased to 0 5 in 22 I (res) while olefinic protons have been decreased to 2.1 indicating thereby their greater reactivities.

TABLE 3—NUMBER OF PROTONS OF THE METHYL ESTERS OF ORIGINAL LINSEED, STAND OILS & EUTECTIC BODIED OILS.

Chemical Shift	Linseed Oil	18	18 S	18 I	19 S	19 I	20	22 S	22 I	22 S (Dist)	22 I (Res)
2.7	0.0	tr	0.0	tr	tr	tr	0.0	0 0	0.0	0.0	0.0
4.4	0.0	tr	tr	0 2	tr	0.3	0.0	0.0	tr	0.0	tr
4.61	4.0	3.0	3.2	2.6	3.2	2.3	3.8	2.5	3.4	2.6	2.1
6.3	3.0	3.0	3.0	3.0	3.0	3.0	3 0	3.0	3.0	3.0	3.0
7.19	3.0	2.2	2.8	1.9	2.3	1.5	1.9	0.75	0.7	1.1	0.5
7.91	6.0	5.4	5.5	5 1	5.2	5 0	6.4	6.2	6.2	6.7	6.6

tr = trace

transesterification using sodium methoxide as catalyst and were distilled at a pressure of 20μ and two fractions, namely, distillate and residue were collected. The original oil and the different fractions of the bodied oils were analyzed in infra-red spectrophotometer (Perkin-Elmer, Model 441). The summary of the infra-red analyses was given in Table 2. The original oil and the different fractions of the bodied oils were

Table 4 shows the proton numbers of the urea-fractions of the methyl esters of stand oils unlike the

TABLE 4—PROTON NUMBERS OF THE UREA FRACTIONS OF THE METHYL ESTERS OF STAND OILS AND EUTECTIC BODIED OILS.

Chemical Shift, τ	Linseed Oil	18 UA	18 UR	19 UA	19 UR	20 UA	20 UR	21 UA	21 UR	22 UA	22 UR
2.7	0.0	0.0	tr	0.0	tr	0.0	0.0	0.0	0.0	0.0	0.0
4.4	0.0	0.0	0.2	0.0	0.3	0.0	0.9	0.0	1.1	0.0	1.6
4.62	4.0	2.0	2.6	2.1	2.8	2.8	3.7	2.3	2.3	1.9	2.5
6.3	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
6.59	0.0	0.0	0.3	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0
7.19	3.0	1.9	1.4	3.0	1.3	1.9	1.5	1.5	1.2	1.4	1.0
7.91	6.0	6.1	5.4	6.0	5.3	6.4	5.5	6.0	5.1	5.8	5.0
8.8 9.2	3.0	3.0	3.0	3.0	2.0	3.0	3.0	3.0	3.0	3.0	3.0

TABLE 5 – NUMBERS OF THE FRACTION OF METHYL ESTERS OF STAND OILS & EUTECTIC BODIED OILS BY COLUMN CHROMATOGRAPHY

Chemical Shift	Linseed Oil	18 M	18 D	18 O	19 M	19 D	19 O	20 M	20 D	21 M	21 D	22 M	22 D
2.7	0.0	0.0	tr	tr	0.0	tr	tr	0.0	0.0	0.0	0.0	0.0	0.0
4.4	0.0	tr	0.6	tr	tr	0.5	tr	tr	2.1	tr	2.5	tr	3.5
4.6	4.0	3.1	4.2	1.8	3.2	4.1	1.7	3.3	3.8	2.8	3.1	2.1	2.6
6.3	3.0	3.0	6.0	3.0	3.0	6.0	3.0	3.0	6.0	3.0	6.0	3.0	6.0
7.19	3.0	2.0	1.8	tr	1.9	1.7	tr	2.1	1.6	1.9	1.8	1.5	2.2
7.91	6.0	6.0	10.1	4.7	6.2	9.8	4.3	6.2	11.1	16.1	11.0	6.0	10.8
8.8 to 9.2	3.0	3.0	6.0	3.0	3.0	6.0	3.0	3.0	6.0	3.0	6.0	3.0	6.0

eutectic bodied oils, all the fractions are free from any aromatic or ether compounds. Like the eutectic bodied oils, all the fractions are free from any cyclohexene ring. The amount of cyclohexene ring increases in time of contact. The cyclohexene proton has been increased to only 0.3 in the nonadduct fraction from eutectic bodied oils but it increased to 1.6 in the corresponding nonadduct fraction from the stand oil. The cyclohexene proton is absent in all the adductable fractions. The diallylic protons have been decreased to 1.6 and 1.2 in the adduct and nonadduct fractions respectively both from stand oil and eutectic bodied oils. The diminution of the α-methylenic protons is not much in all the cases. So, it is evident that Diels-Alder reaction is much prominent in the thermal polymerization rather than the other process. In the eutectic bodied oils, more of polymerization has taken place through the diallylic protons*.

* The comparison is made between the stand oil and eutectic bodied oils which have similar viscosities.

Table 5 shows the proton numbers of the fractions of stand oil esters obtained by column chromatography. All the fractions are free from any aromatic or ether compounds. The amount of cyclohexene protons is much higher in the stand oil e.g. 2.5 in dimer from stand oil and 0.6 in dimer from eutectic bodied oils. The decrease in olefinic protons is also higher in stand oils, e.g. 3.1 in the dimer from the stand oil and 4.0 in the dimer from eutectic bodied oils. One remarkable feature is the large diminution in diallylic protons in the case of eutectic bodied oils, e.g., 1.8 in the monomer and 1.6 in the dimer. This indicates that diallylic protons are more reactive in presence of nitrate salts.

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Some Aspects of Uptake of Manganese by Calcium Hydroxylapatite and the Effect of Such Incorporation on the Solubility of the Bone Mineral.

S. V. CHIRANJEEVI RAO*

Post-Graduate Department of Chemistry, G. M. College, Sambalpur.

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The uptake of manganese by the synthetic calcium hydroyxlapatite is facilitated by increase in Mn^{2} concentration, a decrease in *p*H of medium of exchange and in the particle size of calcium hydroxylapatite. Absorption of Mn^{2} and its accompanying diffusion into the interior of the crystals explain the mechanism of exchange.

CALCIUM hydroxylapatite (CaHA)$Ca_{10}(PO_4)_6(OH)_2$ is the major inorganic component of human skeletal system[1] also called bone mineral. It undergoes a series of cationic and anionic replacement reactions[2]. $Ca^{2+} \rightarrow Mn^{2}$ replacement in CaHA is of extreme biological significance as it explains the mechanism of incorporation of manganese into human skeletal system according to the following equation :

$$Ca_{10}(PO_4)_6(OH)_2 + nMn^{2+} \rightarrow Ca_{10-n}Mn_n(PO_4)_6(OH)_2 + nCa^{2+}$$

So the study of the uptake of manganese by CaHA and the effect of such incorporation on the solubility of bone mineral have been thoroughly investigated with synthetic samples and reported in this paper.

Experimental

Pure and homogeneous sample of CaHA[2] for the study of the dependence of uptake of manganese by CaHA and the samples of CaHA containing varying quantities of manganese in the form of solid solution[3] for the study of the effect of incorporation of manganese in the solubility of bone mineral were prepared by co-precipitation a method specially worked out for this purpose[4]. The chemical composition of these samples were determined[5].

The kinetics of $Ca^{2+} \rightarrow Mn^{2+}$ exchange and the dependence of uptake of manganese by CaHA on factors like *p*H concentration of Mn^{2+} ion, particle sizes were investigated. 0.2g of CaHA was equilibrated with a solution of 100 ml of $Mn(NO_3)_2$(AR) by shaking in air-tight polythene containers, mechanically changing the factors effecting the uptake under investigation each time while other factors were kept constant. The experimental assembly was kept in a thermally insulated cation maintained at 37°±0.5° to simulate biological conditions. At the end of the desired period of equilibration the contents were filtered through $1G_4$ crucible. The residue was washed with doubly distilled water till it was free from the absorbed manganese and the calcium and the manganese contents of the residue were determined[4].

The effect of the incorporation of manganese on the solubility of bone mineral was carried out with the solubility studies being based exclusively on the microanalytical determination of phosphate[6] in the samples after equilibration. Potassium acid phthalate–sodium hydroxide and vernol-HCl were used as buffer combinations. The *p*H was measured with a line-operated Beckman *p*H meter before and after equilibration to ascertain its constancy. 0.2g of the sample (200 mesh, B. S. S) was added to 100 ml of the buffer solution prepared in carbondioxide-free doubly distilled water, contained in air-tight polythene container and shaken mechanically at regulated speed at 37°±0.5°. At the desired period of equilibration the samples were separately filtered through $1G_4$ crucible and the phosphate content in the filtrate was determined complexometrically[6].

Results and Discussion

The results of uptake of manganese by CaHA are given in Fig. 1. The uptake on Mn^{2+} by CaHA is found to (i) decrease with increase of *p*H of the medium of equilibration in the physiologically important range of 5.0 to 8.0, (ii) increase with increase of concentration of Mn^{2+} ion and (iii) increase with decrease in the particle size of CaHA. The uptake of Mn^{2+} is found to be very rapid initially within the first 60 min (8.0 wt%) and remains almost constant thereafter (Fig. 1D). The uptake varies linearly from 11.2 to 15.4 wt% as the concentration of the medium of $Mn(NO_3)_2$ solution increases from 0.01 to 0.1 *M* (Fig. 1B). Fig. 1C shows that the uptake under a given set of experimental conditions increases from 19.2 to 21.8 wt% as the mean radius of the participles decreases from 320μ to 60μ.

* Present address : Chemist, Hindustan Zinc Ltd. Visakhapatnam-15.

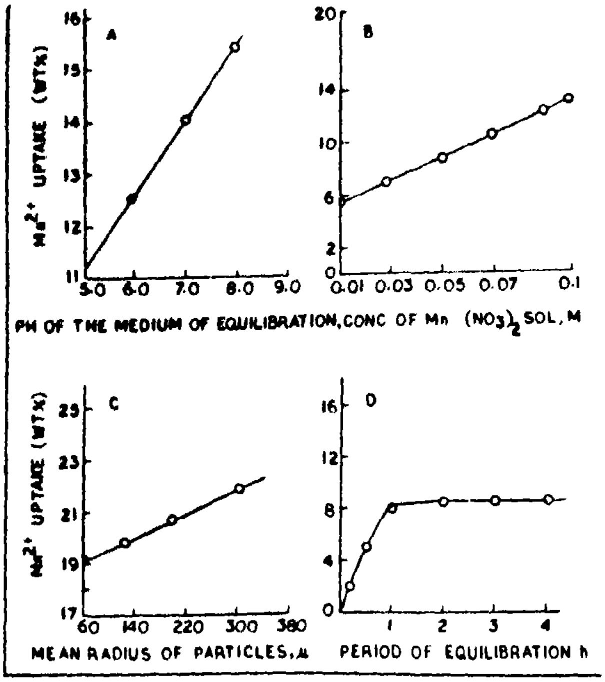


Fig. 1.

The fact that the exchange increases with a decrease in the particle size of CaHA (Fig. 1C) and with an increase in Mn^{2+} concentration (Fig. 1B) leads to the conclusion that the first rapid stage is surface-dependent and the second stage of the exchange may be diffusion-controlled and hence slow.

The results of incorporation of Mn^{2+} on the solubility of bone mineral are given in Fig. 2. The dependence of solubility on (i) the *p*H of medium of equilibration over physiologically important range of 5.0 to 8.0 and (ii) the manganese content in the sample, at a given *p*H was investigated. It was observed that (i) the solubility of given sample decreased with increase of *p*H of the dissolving medium (Fig. 2B), which was due to the proton accepting tendency of $(PO_4)^{3-}$ in the dissolving medium[6] and (ii) at a given *p*H the solubility decreased initially and increased above 40% mole concentration of manganese in the solid solution (Fig. 2A). This observation can be explained on the basis of (i) the common ion effect applied to solubility products of the solid solutions according to Milhofer[7] and (ii) due to the formation of covalent bonds on the introduction of Mn^{2+} in CaHA[8]. This explains the role of incorporation of Mn^{2+} in the solubility of the bone mineral.

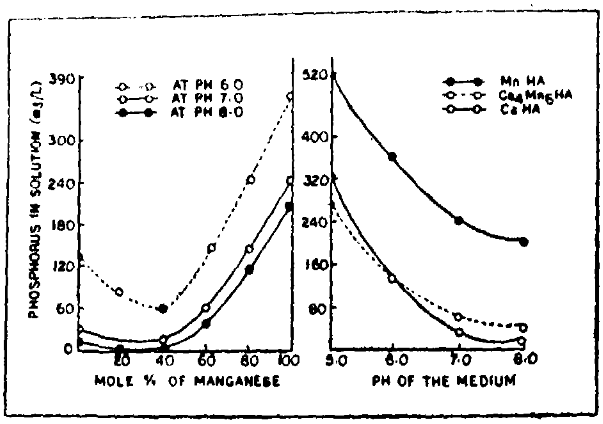


Fig. 2.

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Condensed Thiophene Derivatives, Part-I. Electrophilic Substitution in Benzo [b] Thiophanthrene.

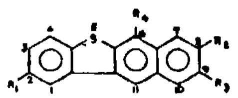
J. N. CHATTERJEA and R. S. GANDHI

Department of Chemistry, Patna University, Patna-800 005.

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Electrophilic substitutions in benzo [b] thiophanthrene have been studied and orientations arrived at. During the work a number of thiophanthraquinones have been unambigously synthesised.

IN a programme on our studies on condensed thiophene derivatives, it became necessary to prepare derivatives of dibenzothiophene and its benzologues of unquestionable orientation. The course of electrophilic substitution in these compounds has not been studied and the present communication deals on the studies on acylation, chloromethylation and bromination of benzo [b] thiophanthrene (I).

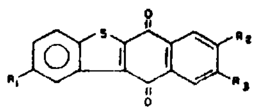


I, $R_1=R_2=R_3=R_4=H$ III, $R_1=R_2=R_3=H$, $R_4=CH_2Cl$

II, $R_1=R_2=R_3=H$, $R_4=COCH_3$ IV, $R_1=R_3=H$, $R_2=R_4=Br$

Friedel-Crafts acetylation of (I) gave a mono acetyl derivative ($\nu_{C=O}$ 1682 cm^{-1}) which on Wolff-Kishner reduction afforded an ethyl benzo [b] thiophanthrene. For the sake of identification 2-, 8-, and 9-ethyl-6, 11-benzo [b] thiophanthraquinones (VI, VII, VIII) were unambiguously synthesised but the reduction of these quinones to the related thiophanthrenes by (a) zinc-dust and ammonia[1], (b) copper-zinc couple and ammonia[2], (c) boiling hydriodic acid[3] and (d) diborane[4] gave either unchanged or interactable products. In the event, the ethyl benzo [b] thiophanthrene in question was oxidised with chromic acid[1] and the resulting product was, to our surprise, identified as the unsubstituted quinone (V) leaving the choice of orientation at either 6-or 11-position. Of these, position 6 is preferred as this is *ortho* to S. The compound is therefore 6-acetylbenzo [b] thiophanthrene (II). Subsequent studies on bromination, as set forth in the sequel, lead to the same conclusion. The result is in contrast to our earlier finding on the oxygen analogue (I, O in place of S) where we obtained a different result[5]. The difference in the electronegativity of the hetero atoms have shown the difference in orientation (+E effect=OR>SR>SeR)[6].

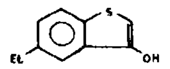
The quinones (VI, VII, VIII) were prepared by standard methods. To illustrate, (VI) was synthesised from ethylbenzene by way of 5-ethyl-3-hydroxythionaphthene (X) which was oxidised to 5-ethylbenzo [b] thiophene-2,3-dione (XI) *via* the related anil[7]. On condensation with phenacyl bromide in alkali (XI) gave the keto-acid (XII) which on cyclisation by way of the acid chloride gave the quinone (VI). Alternatively, the dione (XI) on reaction with chloroacetic acid in alkali gave the dicarboxylic acid (XIII)[1]. The related anhydride (ν_{max} 1770, 1838 cm^{-1}) on Friedel-Crafts reaction with benzene gave 3-benzoyl-5-ethylbenzo [b] thiophene-2-carboxylic acid (XIV) which on cyclisation gave the same quinone (VI). The other quinones with different substituents (ethyl, methyl,



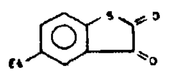
V, $R_1=R_2=R_3=H$ VII, $R_2=Et$, $R_1=R_3=H$

VI, $R_1=Et$, $R_2=R_3=H$ VIII, $R_3=Et$, $R_1=R_2=H$

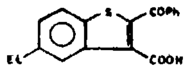
IX, $R_2=Br$, $R_1=R_3=H$



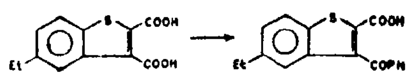
X



XI



XII

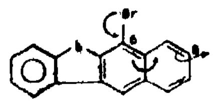


XIII XIV

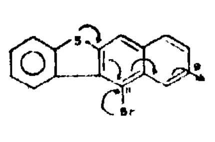
bromine) at different positions were secured essentially by methods illustrated above or by employing minor modifications thereon.

Chloromethylation of (I) gave a mono chloromethyl derivative which on catalytic reduction afforded a methyl thiophanthrene as a light yellow viscous liquid. Here too the orientation was established at 6-position because on oxidation the quinone (V) was again obtained. Thus the chloromethyl compound is established as (III). During this work 2-, 8-,[1] and 9-methy-6, 11-benzo [b] thiophanthraquinones[1] were secured for comparison (*vide* experimental).

The bromination of (I) was very facile and the resulting dibromobenzo [b] thiophanthrene on oxidation gave a monobromo thiophanthraquinone identified as 8 bromo-6, 11-benzo [b] thiophanthraquinone (IX)[1] by direct comparison. The dibromo compound is therefore identified as (IV). It is obvious that the initial substitution of bromine at position 6 has directed the entry of the second bromine atom at position 8 suppressing the influence of the hetero atom S (XV,



XV



XVI

arrows). It is pertinent to point out if the initial entry of the bromine atom were at position 11, then position 9 would be activated (XVI, *arrows*). No 2-or 9-bromothiophanthraquinones could be detected, however, in the residue left in the purification of (IX).

Experimental

All m.ps. or b.ps. are uncorrected. Unless otherwise mentioned, the i. r. spectra were recorded in a Perkin Elmer Infrared spectrophotometer, Model 237 in KBr discs.

Acetylation of Benzo [b] thiophanthrene : A solution of aluminium chloride (1.08 g.) in dry nitrobenzene (10.0 ml.) was added dropwise to a well stirred ice cold (0-2°) mixture of benzo [b] thiophanthrene (1 0 g.), acetyl chloride (0 4 ml.) and tetrachloroethane (10.0 ml) over a period of 20 min. The temperature was maintained at 0-2° for further 20 min. with constant shaking. On keeping the reaction mixture in a refrigerator for 48 hrs., an orange complex gradually separated which was decomposed with crushed ice-hydrochloric acid (5*N*). The solvents were removed by steam distillation. A light yellow mass, which separated, was taken up in benzene, washed, dried and finally chromatographed on an activated alumina column. Five fractions were collected with benzene as an eluent. The second to fifth fractions gave pure 6-acetylbenzo [b] thiophanthrene (II ; 0.6 g). The ketone crystallised from benzene in short yellowish needles, m.p. 91-93°. (*Found* : C, 78 30 ; H, 4.41. $C_{18}H_{12}OS$ requires : C, 78.25 ; H, 4.38%). i.r. spectrum $\nu_{C=O}$ 1682 cm^{-1}, ν_{C-S} 704 cm^{-1}.

The *oxime* crystallised from MeOH in light yellow crystals, m.p. 149-50°. (Found : C, 74.12 ; H, 4 68 ; N, 4.79. $C_{18}H_{13}NOS$ requires : C, 74.21 ; H, 4.50 ; N, 4.81%).

Wolff-Kishner Reduction of 6-Acetylbenzo [b] thiophanthrene : The above acetyl compound (1.0 g.) in dry diethylene glycol (10.0 ml.) was treated with hydrazine hydrate (2.0 ml. ; 99-100%) and boiled for 2 hrs. On cooling, the colourless *hydrazone* separated out. To this, pot. hydroxide (2.0 g.) was added after removing water from the system by distillation and heated to 190-200° for 3 hrs till evolution of nitrogen ceased. The mixture was cooled to r.t. and diluted with water and the oily layer extracted with ether, washed, dried and distilled under reduced pressure at 140 50°/1 mm. to give a light yellowish liquid, 6-ethylbenzo [b] thiophanthrene (0 8 g.). (Found : C, 82.39 ; H, 5.36. $C_{18}H_{14}S$ requires : C, 82.42 ; H, 5.38%).

The *2,4,7-trinitrofluorenone* complex was crystallised from benzene in orange-red crystalline mass, m.p. 192-93°. (Found : N, 7.26. $C_{18}H_{14}S.C_{13}H_5N_3O_7$ requires : N, 7.28%).

Oxidation of 6-ethylbenzo [b] thiophanthrene : A solution of 6-ethylbenzo [b] thiophanthrene (0.53 g.) in a minimum volume of AcOH (3.0 ml.) was treated with a solution of chromic acid (0.55 g.) in a minimum volume of water, boiled for ½ min. The colour of the solution changed to yellowish-green. After cooling and diluting with water, a yellow quinone separated out on scratching. This was extracted with benzene, dried over $MgSO_4$ and chromatographed on an activated alumina column in benzene. Yellow needles of 6,11-benzo [b] thiophanthraquinone (V ; 0.1 g.) were obtained on concentration and subsequent crystallisation from AcOH. It was identified by m.p., mixed m.p. (212-13° ; no depression) and i.r. spectrum. (Found : C, 72.81 ; H, 3.08. Calc. for $C_{16}H_8O_2S$: C, 72.73 ; H, 3.05%). i.r. Spectrum : 1,4-quinone absorption at 1665 cm^{-1}, and ν_{C-S} band at 702 cm^{-1}).

Bromination of Benzo [b] thiophanthrene : A solution of bromine (0.4 ml.) in AcOH (2.0 ml.) was added dropwise to a solution of benzo [b] thiophanthrene (1.17g.) in AcOH (10.0 ml.) over a period of 20 min with constant stirring. The mixture was kept at r.t. for 6 hrs. *6,8-Dibromobenzo [b] thiophanthrene*, which was separated out, was collected, washed with EtOH and crystallised from AcOH in colourless plates, m.p. 180-81°. (Found : C, 48.89 ; H, 2.16. $C_{16}H_8Br_2S$ requires : C, 48.99 ; H, 2.06%).

Oxidation of 6,8-Dibromobenzo [b] thiophanthrene : Chromic acid (0.5 g) dissolved in minimum volume of water (3 drops) was added to 6,8-dibromobenzo [b] thiophanthrene (0.8 g.) also dissolved in minimum volume of AcOH (9.0 ml.). The mixture was gently boiled for ½ min. and diluted with water to give 8-bromo-6, 11-benzo [b] thiophanthraquinone (IX), which was purified by chromatography over an alumina column. 8-Bromoquinone crystallised from AcOH in silky yellow needles (0.3 g.), m.p. 219-20°. On treatment with conc. sulphuric acid a dark violet colour was obtained. (Found : C, 55.82 ; H, 2.07. $C_{16}H_7BrO_2S$ requires : C, 55.98 ; H. 2.04%). i.r. Spectrum : 1,4-quinone absorption at 1660 cm^{-1} and ν_{C-S} band at 700 cm^{-1}.

Identification of this quinone was confirmed by m.p. and mixed m.ps. and comparison of i.r. spectrum with an authentic sample.

Reductive Acetylation of 8-Bromo-6, 11-benzo [b] thiophanthraquinone : A mixture of foregoing bromoquinone (0.1 g), zinc-dust (0.08 g), acetic anhydride (3 2 ml.) and fused sod acetate (0.32 g.) was refluxed for 3 hrs. The colourless solution was poured into wat r and the residual zinc extracted with small quantities of AcOH. *8-Bromobenzo [b] thiophanthrene-6, 11-diacetate* was collected and crystallised from AcOH in elongated colourless needles (0.07 g.), m p. 207-08°. (Found : C, 55.88 ; H, 3 02. $C_{20}H_{13}BrO_4S$ requires : C, 55.94 ; H, 3.03%).

Chloromethylation of Benzo [b] thiophanthrene : A rapid stream of dry hydrogen chloride gas was passed into a vigorously stirred mixture of benzo [b] thiophanthrene (2.0 g.) and aqueous formaldehyde solution (6.0 ml. ; 40%) till the mixture was saturated. During this period, temperature of the mixture raised to 60-65°. This temp. was maintained for $1\frac{1}{2}$ hrs. while a slow stream of dry hydrogen chloride gas was continuously passed into the mixture which was cooled and diluted with water, the viscous mass was extracted with ether and washed successively with water, sod. bicarbonate solution (10%) and water. After drying over $MgSO_4$ and removal of solvent, a yellowish material was obtained. *6-Chloromethylbenzo [b] thiophanthrene* crystallised from EtOH in cream colour plates (2.4 g.), m.p. 182-83°. (Found : C, 72.09 ; H, 3.91. $C_{17}H_{11}ClS$ requires : C, 72.21 ; H, 3.89%).

Catalytic Reduction of 6-Chloromethylbenzo [b] thiophanthrene : 6-Chloromethyl derivative (2.0 g.) was catalytically hydrogenated at the r.t. and ordinary pressure in the presence of palladised charcoal (0.5 g. ; 30%) in ethyl acetate (20.0 ml.) containing potassium hydroxide (0.1 g) in water (1.0 ml). Hydrogenation was complete with the absorption of one mole hydrogen over a period of 4-5 hrs. The solvent was removed and the residual oil distilled at 200-240°/2 mm. to give *6-methylbenzo [b] thiophanthrene* (1.1 g.) as a liquid, which did not solidify on keeping in a refrigerator even for a long time. (Found : C, 82.16 ; H, 4.98. $C_{17}H_{12}S$ requires : C, 82.24 ; H, 4.87%).

Oxidation of 6-methylbenzo [b] thiophanthrene : The above thiohydrocarbon (0.52 g.) was dissolved in minimum volume of glacial AcOH (2.0 ml.) and added to a solution of chromic acid (.55 g.) in water (4 drops) and boiled for $1\frac{1}{2}$ min. On work up a yellow solid separated (0.1 g.) which was identified as 6, 11-benzo [b] thiophanthraquinone, m.p. 212-13°, (identical i.r. spectra). (Found : C, 72.76 ; H, 3.12. Calc. for $C_{16}H_8O_2S$: C, 72.73 ; H, 3.05%).

5-Ethylbenzo [b] thiophene-2,3-dione (XI) : A solution of oxalyl chloride (6.0 ml.) in dry ether (15.0 ml.) was added dropwise to a well-cooled solution of 4-ethylthiophenol[8] (6.9 g.) in dry ether (40.0 ml.) and kept at r.t. till the initial evolution of hydrogen chloride ceased. It was then refluxed for 1 hr. The excess of oxalyl chloride was removed by treating thrice with dry ether and their subsequent removal under reduced pressure. The residual oil was taken up in carbon disulphide (40.0 ml.) and then anhydrous aluminium chloride (15.0 g.) was added in small portions over a period of 1 hr. at 0° ; after leaving it for 3 hrs. at r.t. the mixture was refluxed for 3 hrs. The *dione* crystallised from AcOH, m p. 110 11° ; yield 90%. (Found : C, 62.48 ; H, 4.22. $C_{10}H_8O_2S$ requires : C, 62.50 ; H, 4.20%). i.r. Spectrum : 1,4-quinone absorption at 1715 cm^{-1}, ν_{C-S} band at 799 cm^{-1}.

5-Methylbenzo [b] thiophene-2,3-dione : was prepared according to the method described by Papa, Schwenk and Ginsberg[9].

5-Bromobenzo [b] thiophene-2,3-dione : 5-Bromobenzo [b] thiophene-2,3-dione was prepared following the method of Harley-Mason and Mann[8]. For this 3-hydroxy-5-bromobenzo [b] thiophene[10] (5-bromothioindoxyl ; 5.0 g.) was dissolved in boiling NaOH solution (50.0 ml. ; 5%), cooled down to 60°. To this was added, with stirring, a solution of *p*-nitrosodimethylaniline (5.0 g.) in dilute hydrochloric acid (30.0 ml. ; 5%), keeping the temp. at 60°. The violet *anil* separated rapidly on cooling. After leaving for 12 hrs., the *anil* was collected and thoroughly washed successively with cold water, dilute hydrochloric acid (2*N*), hot and cold water and dried ; yield 5.0 g. The anil was boiled with hydrochloric acid (100.0 ml. ; 15%) for 4 hrs and filtered after cooling. The undissolved residue was washed with water and digested with an excess of boiling sod. carbonate solution (50%) for 30 min. The hot mixture was filtered into crushed ice and then acidified to give 5-bromobenzo [b] thiophene-2, 3-dione (4.1 g) which was collected, washed with water and crystallised from MeOH in reddish-brown needles, m.p. 177-78°. (Found : C, 39.57 ; H, 1,33. $C_8H_3BrO_2S$ requires : C, 39.51 ; H, 1.23%).

2-Benzoyl-5-ethylbenzo [b] thiophene-3-carboxylic Acid (XII) : Ethanol was added to a mixture of 5-ethylbenzo [b] thiophene-2,3-dione (2.0 g.), phenacyl bromide (4.0 g.) and NaOH solution (25.0 ml. ; 2*N*) till all went into solution. The mixture was then refluxed for 7-8 hrs., cooled, filtered, solvent removed and acidified with conc. hydrochloric acid to give 2-benzoyl-5-ethylbenzo [b] thiophene-3-carboxylic acid (2.2 g.), m.p. 115-17°. The compound gave an orange-red colouration with conc. sulphuric acid. (Found : C, 69.65 ; H, 4.57. $C_{18}H_{14}O_3S$ requires : C, 69.67 ; H, 4.55%). i.r. Spectrum : Aryl ketone absorption at 1668 cm^{-1}, carboxylic acid at 1688 cm^{-1}, ν_{C-S} at 690 cm^{-1}.

The synthesis of the following keto-acids was effected by an unambiguous route as described above.

2-Benzoyl-5-bromobenzo [b] thiophene-3-carboxylic Acid crystallised from AcOH in colourless needles, m.p. 220-21°, giving an orange colour with sulphuric acid. (Found : C, 53.20 ; H, 2.51. $C_{16}H_9BrO_3S$ requires : C, 53.19 ; H, 2.49%).

2-Benzoyl-5-methylbenzo [b] thiophene-3-carboxylic Acid: crystallised from AcOH in short colourless needles, m.p. 234-35°. It gave an orange colouration with conc. sulphuric acid (Found : C, 68.88 ; H, 4.09. $C_{17}H_{12}O_3S$ requires : C, 68.91 ; H, 4.08%).

2-Ethyl-6,11-benzo [b] thiophanthraquinone (VI) : 2-Benzoyl-5-ethylbenzo [b] thiophene-3-carboxylic acid (0.5 g.) was converted into the acid chloride by dissolving in thiophene-free benzene (10.0 ml.) and adding thionyl chloride (0.25 ml.) followed by catalytic amount of dry pyridine. A clear solution was obtained after refluxing for 3 hrs. After removing benzene and excess of thionyl chloride under reduced pressure, carbon disulphide (15.0 ml.) was added to the brown oily mass, cooled down to 0° and aluminium chloride (1.5 g.) was added slowly. The quinone crystallised from AcOH in yellow needles (0.21 g.), m. p. 156-57°. The compound imparted a dark violet colour to conc. sulphuric acid. (Found : C, 73.94 ; H, 4.19. $C_{18}H_{12}O_2S$ requires : C, 73.96 ; H, 4.14%). i.r. Spectrum : 1.4-Quinone absorption at 1655 cm^{-1} and $\nu_{C\ S}$ band at 700 cm^{-1}. The most obvious route to 2-bromo- and 2-methyl quinones is by an adaptation of methods as used above.

2-Bromo-6,11-benzo [b] thiophanthraquinone (IX) : crystallised in fine yellow needles, m. p. 222-23°, imparting a violet colouration on treatment with conc. sulphuric acid. (Found : C, 55.99 ; H, 2.11. $C_{16}H_7BrO_2S$ requires : C, 55.98 ; H, 2.04%).

2-Methyl-6,11-benzo [b] thiophanthraquinone : crystallised in silky yellow needles, m. p. 188°, giving a violet colouration with conc. sulphuric acid. (Found : C, 73.48 ; H, 3.82. $C_{17}H_{10}O_2S$ requires : C, 73.38 ; H, 3.62%).

3-Benzoyl-5-ethylbenzo [b] thiophene-2-carboxylic Acid (XIV): 5-Ethylbenzo [b] thiophene-2,3-dione (1.47 g.) was dissolved in sod. carbonate solution (30.0 ml. ; 2*N*) and heated on water-bath at 50-60° ; a solution of chloroacetic acid (0.68 g.) neutralised with sod. carbonate solution (10%) was added slowly and the mixture heated on water-bath at 70-75° for ½hr. It was cooled down and acidified with conc. hydrochloric acid ; the *4-ethyl-2-glyoxylic-phenylthioglycolic acid* which precipitated out, was filtered. The reddish crystalline mass was crystallised from benzene in colourless needles (0.9 g.), m p. 144-46°. (Found : C, 53.75 ; H, 4.61. $C_{12}H_{12}O_5S$ requires : C, 53.73 ; H, 4.51%). This *thioglycolic acid* (0.9 g.) was cyclised by fusing with NaOH (15.0 ml. ; 100%) on an oil-bath at 200° for about ½hr. till the yellow colour turned practically colourless. The mass was collected, dissolved in water and *5-ethylbenzo [b] thiophene-2, 3-dicarboxylic acid* (XIII ; 0.7 g.) was obtained on acidification with conc. hydrochloric acid. It was crystallised from a large volume of hot water in pale yellow elongated needles (0.6 g.), m.p. 194-96°. (Found : C, 53.67 ; H, 5.05. $C_{12}H_{10}O_4S.H_2O$ requires : C, 53.73 ; H, 4.51%). The foregoing dicarboxylic acid (0.6 g.) was dissolved in acetic anhydride (4.0 ml.) and refluxed for 2½ hrs. The anhydride was removed by distillation under reduced pressure. On cooling, fine light yellow needles of *5-ethylbenzo [b] thiophene-2, 3-dicarboxylic anhydride* (0.55 g.) were obtained, m.p. 130-31°. (Found : C, 62.12 ; H, 3.51. $C_{12}H_8O_3S$ requires : C, 62.07 ; H, 3.47%). i. r. Spectrum : Anhydride absorption at 1770 cm^{-1}. The above *anhydride* (0.55 g.) was dissolved in thiophene-free benzene (10.0 ml.) and cooled down to 0°, then aluminium chloride (2.0 g.) was added to it in parts over a period of 15 min. and left overnight. Next day, it was boiled for 1 hr., cooled and decomposed with crushed ice-hydrochloric acid (5*N*). *3-Benzoyl-5-ethylbenzo [b] thiophene-2-carboxylic acid* (XIV ; 0.2 g.) crystallised from AcOH in colourless needles, m. p. 158-60°. (Found : C, 69.59 ; H, 4.56. $C_{18}H_{14}O_3S$ requires : C, 69.67 ; H, 4.55%). i.r. Spectrum : Aryl ketone absorption at 1665 cm^{-1}, carboxyl carbonyl at 1680 cm^{-1} & $\nu_{C\ S}$ band at 690 cm^{-1}.

The following compounds were also obtained using the above described procedure.

4-Methyl-2-glyoxalic-phenylthioglycolic Acid crystallised in light yellow crystals, m.p. above 300° ; (Found : C, 51.81 ; H, 4.11. $C_{11}H_{10}O_5S$ requires : C, 51.97 ; H, 3.97%).

5-Methylbenzo [b] thiophene-2,3-dicarboxylic Acid crystallised in pale yellow needles, m. p. 246-47° (decomp.). (Found : C, 51.86 ; H, 3.85. $C_{11}H_8O_4S.H_2O$ requires : C, 51.97 ; H, 3.97%).

5-Methylbenzo [b] thiophene-2, 3-dicarboxylic Anhydride crystallised in fine light silky yellow needles, m. p. 208-10°. (Found : C, 60.43 ; H, 2.61. $C_{11}H_6O_3S$ requires : C, 60.56 ; H, 2.77%).

3-Benzoyl-5-methylbenzo [b] thiophene-2-carboxylic Acid crystallised in colourless needles, m. p. 202-03°. On treatment with conc. sulphuric acid it gave an orange colour. (Found : C, 68.81 ; H, 4.12. $C_{17}H_{12}O_3S$ requires : C, 68.91 ; H, 4.08%).

2-Ethyl-6, 11-benzo [b] thiophantraquinone (VI) : 3-Benzoyl-5-ethylbenzo [b] thiophene-2, carboxylic acid (1.0 g.) was dissolved in thiophene-free benzene (10.0 ml.) and thionyl chloride (0.5 ml.) was added at r. t. followed by one drop of pyridine. After leaving for 15 min., it was refluxed for 3 hrs. on the water-bath. The excess of thionyl chloride was removed under reduced pressure. The brown oily mass was taken up in dry carbon disulphide (25.0 ml.) and cooled to 0° and powdered aluminium chloride (2.5 g.) was added and the whole mass was kept overnight at the r.t. The quinone (VI) crystallised in yellow needles (0.65 g.), m.p. 156-58°, identical with the quinone prepared by the previous method (Found : C, 73.88 ; H, 4.23. Calc. for $C_{18}H_{12}O_2S$: C, 73.96 ; H, 4.14%). By similar method, 2-Methyl-6, 11-benzo [b] thiophanthraquinone (m.p. 188-89°) was also prepared from 3-benzoyl-5-methylbenzo [b] thiophene-2-carboxylic acid. (Found : C, 73.58 ; H, 3.74. Calc. for $C_{17}H_{10}O_2S$: C, 73.48 ; H, 3.62%).

3-(4'-Ethylbenzoyl) benzo [b] thiophene-2-carboxylic Acid: Benzo [b] thiophene-2,3-dicarboxylic anhydride[1] (2.04 g.) was taken up in freshly distilled ethylbenzene (15.0 ml.) and cooled down to 0° ; then anhydrous aluminium chloride (5.0 g.) was added to it in small portions over a period of 30 min. The reaction mixture was kept overnight in a refrigerator, when an orange coloured aluminium-complex gradually formed which was decomposed with hydrochloric acid (5*N*). The *acid* crystallised from AcOH in short colourless needles, m.p. 199-200° giving an orange colouration to sulphuric acid, yield 1.21 g. (Found: C, 69.63 ; H, 4.65. $C_{18}H_{14}O_3S$ requires: C, 69.67 ; H, 4.55%). i.r. Spectrum: Aryl ketone absorption at 1668 cm^{-1} & carboxyl carbonyl at 1688 cm^{-1}.

8-Ethyl-6,11-benzo [b] thiophanthraquinone (VII): 3-(4'-Ethylbenzoyl) benzo [b] thiophene-2-carboxylic acid (1.56 g.) was dissolved in thiophene-free benzene (15.0 ml.) and thionyl chloride (0.5 ml.) was added to it followed by one drop of dry pyridine. It was refluxed for 3 hrs. till a clear solution was obtained. After removing last traces of thionyl chloride under reduced pressure, the brown liquid was dissolved in dry carbon disulphide (15.0 ml.). Powdered aluminium chloride (5.0 g.) was added to it in portions and the resulting reaction mixture was kept overnight at r.t. The *quinone* crystallised from AcOH in short yellow needles (1.0 g.), m.p. 138-39°. It gave a dark violet colouration to sulphuric acid. (Found: C, 74.01 ; H, 4.23. $C_{18}H_{12}O_2S$ requires: C, 73.96 ; H, 4.14%). i.r. Spectrum: 1,4-Quinone absorption at 1622 cm^{-1}.

2-(4'-Ethylbenzoyl) benzo [b] thiophene-3-carboxylic Acid: A mixture of aqueous ethanolic sodium hydroxide solution of benzo [b] thiophene-2,3-dione (3.4 g.) and 4-ethylphenacyl bromide (4.6 g.) was refluxed for 3 hrs. and cooled. Ethanol was boiled off and the residue filtered and acidified to give the desired *keto-acid*, which was crystallised from AcOH in short needles, m.p. 223-24°, yield 5.25 g. It imparted an orange colour to conc. sulphuric acid. (Found: C, 69.52 ; H, 4.81. $C_{18}H_{14}O_3S$ requires: C, 69.67 ; H, 4.55°/₀).

2-(4'-Bromobenzoyl) benzo [b] thiophene-3-carboxylic Acid crystallised in shining short needles, m.p. 230-31°. An orange colouration was obtained on treatment with conc. sulphuric acid. (Found: C, 53.12 ; H, 2.52. $C_{16}H_9BrO_3S$ requires: C, 53.19 ; H, 2.49°/₀).

9-Ethyl 6,11-benzo [b] thiophanthraquinone (VIII): The foregoing *keto-acid* (0.5 g.) was converted into its acid chloride by dissolving it in thiophene-free benzene (10.0 ml.) and adding thionyl chloride (0.25 ml.) followed by catalytic amount of dry pyridine. A clear solution was obtained after refluxing for 3 hrs. and cyclised as before with anhydrous aluminium chloride (1.5 g.). The *quinone* crystallised from AcOH in beautiful yellow needles, yield 0.21 g., m.p. 166-67°, giving a reddish-violet colouration to conc. sulphuric acid. (Found: C, 73.91 ; H, 4.21. $C_{18}H_{12}O_2S$ requires: C, 73.96 ; H, 4.14°/₀). i.r. Spectrum: 1,4-Quinone absorption at 1657 cm^{-1}, ν_{C-S} band at 690 cm^{-1}.

9-Bromo-6, 11-benzo [b] thiophanthraquinone crystallised in beautiful silky yellow needles, m.p. 246-47°, was also synthesised following the above method. It gave a dark violet colouration to conc. sulphuric acid. (Found: C, 55.83 ; H, 2.11. $C_{16}H_7BrO_2S$ requires: C, 55.98 : H, 2.04°/₀).

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Double Boundary Formation on Electrolysis in a W-tube : Theory and its Verification

SUSANTA K. SENGUPTA and SANTI R. PALIT

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32

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Electrolysis in W-tube type cells has earlier been reported to result in the formation of two sharp and stationary boundaries separating the entire electrolyte into three distinct zones, coloured alkaline, neutral water and coloured acidic (for coloured electrolytes). Herein, a theory has been offered in terms of 'sweeping out of one ion by another' to explain this double boundary formation phenomenon. A number of experimental consequences and confirmations of the theory have been discussed.

IT has been reported by Palit[1,2] that electrolysis of coloured electrolytes (for example, dyes and potassium dichromate solutions) in W-tube type cells results in formation of two sharp and stationary boundaries P and Q (as shown in Figure 1) dividing the entire solution into three zones of contrasting colour and pH—coloured alkaline (CP), colourless neutral water (PQ) and coloured acidic (QA). The phenomenon referred to as 'double boundary formation' has been found to be a usual feature of electrolysis in W-tube type cells. Herein a mechanism has been advanced to explain this novel observation in terms of 'sweeping out' of ions of the electrolyte by ions of the solvent (viz. protons and hydroxyl ions in the case of aqueous systems).

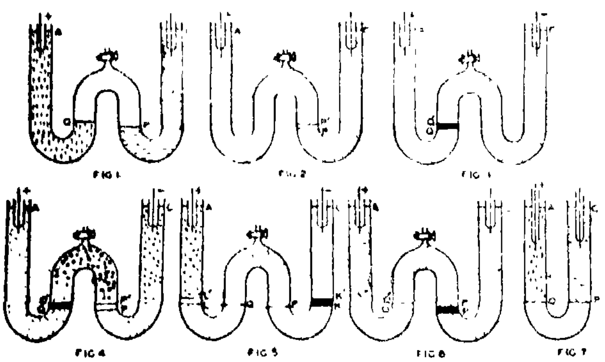

FIG 1 FIG 2 FIG 3

FIG 4 FIG 5 FIG 6 FIG 7

Theory

Ion Migration Pattern—— Consequent on electrolysis of an electrolyte (MX) like, potassium dichromate, acid and alkali are generated at the anode and cathode respectively. Now, within a short time the acid and alkali get uniformly mixed-up entirely in their respective vertical electrode limbs and somewhat beyond upto the two points P and Q. This can be tested using indicators. Thus at Q and P two boundaries—one between acidic/neutral and the other between neutral/alkaline solutions, get developed. As electrolysis continues, more and more acid and alkali are liberated and within a short time they get uniformly distributed in the corresponding electrode limbs but only up to the points Q and P respectively. Thus the boundaries at these two points remain stationary on continuation of the electrolysis. As the solution is further electrolysed, the regions AQ and PC become increasingly concentrated in acid and alkali respectively whereas the central region QP maintains practically the same ionic strength and pH as at the initial state. The situation remains so as long as the current carriers are ions of the original electrolyte. However, after a period, the duration of which depends on the ionic strength of the original electrolyte and the current strength at which it is being electrolysed, a state is reached when the protons in AQ and hydroxyl ions in PC attain sufficient charge-transport capacity to make a substantial contribution to the total charge-carriers. As electrolysis proceeds, these two ions increasingly take part in the conduction of current at least in AQ and PC, and a stage is reached when a very high percentage of the total current is transported by these two ions. In course of the above physical processes associated with electrolysis, zones of varying conductances are being formed giving rise to varied distribution of potential gradient across the entire cell.

Let us now examine what would happen in the intermediate region bounded by P and Q when the protons in AQ and hydroxyl ions in PC become the predominant charge carriers. So long the sole carriers are ions of the original electrolyte, equal number of the same ions are getting in and getting out of this region and as such the region records no change. But as soon as the protons and hydroxyl ions take over the current transport in AQ and PC respectively, the situation in PQ also starts changing. Now, across P enters a flow of negative charge comprising X^- and OH^-, whereas the charge that is swept out across P consists purely of X^-. Thus at the onset of this process, a very thin lamina of solution (containing carried over X^- and OH^-) sandwiched between neutral and alkaline electrolytes, can be conceived to be formed at P. In the next stage, two things could happen. Firstly the layer just above

that at P will attain the anionic composition of that at P in the above way and secondly the layer at P will now have an anionic composition with a higher-fraction of OH^-. Thus as electrolysis proceeds, the thin layer of mixed anionic composition would be advancing and expanding towards Q, and at the same time getting more and more enriched in OH^- and depending on the current strength and anionic composition, a time will be reached when the anions in the entire PQ zone will be almost all OH^- ions. In other words the advancing OH^- ions would as it were be sweeping out the other anions from the intermediate zone PQ. This advancement can proceed only upto Q as beyond it the only anion under the present system that can exist is X^- and across the boundary at Q a change in the anionic current carrier occurs because OH^- ions are coming in and gets replaced by an equivalent number of X^-ions.

Simultaneously with the above process a similar sequence of events takes place at Q in which protons gradually take over the cationic current carriage from M^+ ions and eventually sweep out the cations. As a consequence the zone PQ would eventually contain almost exclusively protons and hydroxyl ions and this zone remains separated from the catholyte CP and anolyte AQ by demarcation of two boundaries at P and Q. Thus the zone PQ is virtually a water zone (trace ionic impurities may be admixed) and the major part of the applied voltage drops over this region and the current reading falls to a low value. So, the whole solution gets now stratified into the three zones viz. the alkaline catholyte (CP), neutral water (PQ) and acidic anolyte (QA) demarcated by the two sharp boundaries at P and Q ; for potassium dichromate the colour sequences would be lemon yellow-colourless-orange yellow as observed in practice.

Experimental

Some direct experimental consequences and confirmations of the above theory of double boundary formation are discussed below.

(i) *Colourless band formation at P* : If some highly concentrated electrolyte having the anion different from X^- be added at cathode before beginning the electrolysis, our theory predicts that a thin band of solution enriched with the new anion but depleted in X^- should be formed just above P on electrolysis and this will then advance and extend upto Q. This has been confirmed by adding concentrated H_2SO_4, Na_2SO_4 or NaOH at cathode to dilute $K_2Cr_2O_7$ solution when within a few seconds of the start of electrolysis a distinctly visible perfectly colourless thin band (PP′) forms at P (Fig. 2). With further electrolysis, this band expands up to Q when the entire section PQ becomes colourless.

(ii) *Deep coloured band formation at Q* : If the above operation be done at the anode, the theory predicts that a thin band of a solution enriched with X^- should develop at Q. The layer should also get more and more enriched with X^- with electrolysis. This has been confirmed by adding the aforementioned electrolytes to dichromate solution at anode when a thin band of orange colour (Q′Q) makes its appearance at Q within few seconds of the start of electrolysis (Fig. 3.). With time the band gets deeper and deeper. Of course this accumulation stops with exhaustion of dichromate ion in the QC area, when the deep band expectedly smears out into the QA area to have a uniform shade (since the ions that would be swept out from this deep band section are X^- ions).

(iii) *Double band formation* : In fact, if such extra electrolyte addition be made both at the cathode and the anode, the deep band (Q′Q) at Q as well as the colourless band (PP′) at P appears in a few seconds simultaneously on switching on the electrolysis (Fig 4). It is obvious that such electrolyte addition at one or both the electrodes provides us with a technique for quick double boundary formation (about 30 minutes against several hours or overnight by the usual method).

(iv) *Band formation in outermost limbs* : If initially the section KPQL (vide Fig. 5) be filled with a mixture of the coloured electrolyte (e. g. potassium dichromate) and concentrated additional electrolyte (e. g. sodium sulphate), the rest being filled with the dichromate solution alone, and the system be electrolysed, the theory predicts the following. A colourless lamina (L′L) at L and a concentrated band (KK′) at K should appear. The point has been borne out by experiments (Fig. 5). Also as expected from the theory, the development of such a coloured or colourless thin band does not occur, if the entire solution be initially a mixture for example of potassium dichromate and sodium sulphate.

(v) *Band formation (colourless at Q and deep coloured at P)* : If the cell be filled up with a cationic dye solution (for visual demonstration purpose) and an additional electrolyte like concentrated sodium sulphate at cathode or anode or both be added as in (i), (ii) or (iii), a deep coloured band (PP′) at P or a colourless band (Q′ Q) at Q or both (as the case may be) are expected from theory. This has been confirmed experimentally with crystal violet solution (Fig. 6).

(vi) *Deionization in the central zone* : In only those systems where protons from the anodic section and hydroxyl ions from the cathodic section can partake in sweeping out cations and anions respectively in the PQ zone, the current reading should record a gradual fall during the build-up of double-boundary formation. This has also been verified experimentally.

(vii) *Double boundary formation in a simple U-tube* : Suppose the bend section of a simple U-tube (PQ of Fig. 7) be filled with a coloured electrolyte

such as potassium dichromate to which enough sugar has been added to make the solution sufficiently heavy and the rest be filled with the same dichromate solution without sugar to make a sharp separation at P and Q, and the system be electrolysed. According to the foregoing reasoning it should result in double boundary formation in which the section PQ would be colourless (Fig. 7), as now the alkaline/neutral and neutral/acidic boundaries could form at P and Q respectively. This has been found to be so experimentally. Further as expected, this double boundary formation can be quickened by adding extra electrolyte such as sodium sulphate at the cathode (in the case of a coloured anion) in the same way as in a W-tube.

The mechanism thus proposed in term of 'sweeping out' of the ions in the intermediate zone by other ions (usually H^+ and OH^- unless others are intentionally added) in the other zone, explains satisfactorily all salient features associated with electrolysis in W-tube type cells and predicts a few novel results which have also been experimentally confirmed.

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Substituted 1-Arylaminomethyl-5,6-dimethylbenzimidazoles and Related Products.

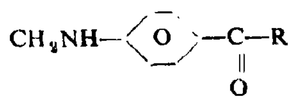
RAJENDRA S. VARMA

Department of Chemistry, Lucknow University, Lucknow 226007

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A series of 1-arylaminomethyl-5, 6-dimethylbenzimidazoles (IV) and other derivatives have been synthesised from 5, 6-dimethyl-benzimidazole.

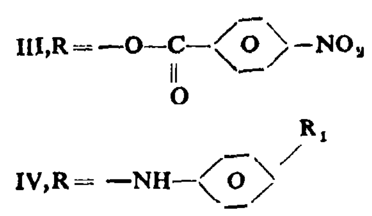
It has been observed that cyanocobalamin and folic acid are essential for the growth of certain micro-organisms. The presence of 5, 6-dimethylbenzimidazole nucleus in the structure of vitamin B_{12} has led to the synthesis of several benzimidazole derivatives such as 5-methyl ; 4,5-dimethyl and 2,5-dimethyl benzimidazoles as antagonists of this vitamin[1]. In view of these observations it was considered of interest to design a number of compounds (I, II, III and IV) derived from 5,6-dimethylbenzimidazole as antagonists of B_{12}. Certain compounds (IV) described in this article may also be regarded as antagonists of folic acid because they incorporate



group present in folic acid.

I, R = OH

II, R = O—C(=O)—Me



1-Hydroxymethyl-5, 6-dimethylbenzimidazole (I) was obtained by the treatment of formaldehyde with 5,6-dimethylbenzimidazole. Acetylation of I with acetic anhydride furnished II. When I was allowed to react with 4-nitrobenzoyl chloride there was obtained III. Various 1-arylaminomethyl-5,6-dimethylbenzimidazoles (IV) were prepared by two methods. In one procedure, 5,6-dimethylbenzimidazole, aqueous formaldehyde and an appropriate primary amine were condensed to yield IV. Direct condensation of I with amines comprised the other method. When a compound was prepared by employing both the procedures its identity was always checked by the comparison of m.p., m.m.p. and i.r. spectra.

I,II,III and IV thus synthesised were characterised by their satisfactory elemental analyses. Additional evidence was derived from their i.r. and n.m.r. spectral data. Characteristic i. r. bands were present in the spectra of I,II,III and IV (1,7,8,11,12 ; Table 1). The n m r. spectrum of 10 was in accord with the assigned structure. Two sharp singlets at δ 2.33 and 3.73 have been attributed to two methyl and one methoxyl protons, respectively. The signal due to CH_2 and NH observed at δ 5.36 as a broad band integrated for three protons. After D_2O exchange the integration of this signal indicated only two protons. Absorptions due to aromatic protons occurred at δ 6 66 (four protons at 3′,4′,5′,6′), 7.16 (2-H) and 7.4-7.9 (two protons at 4 and 7 positions).

TABLE 1—1-ARYLAMINOMETHYL-5,6-DIMETHYLBENZIMIDAZOLES(IV)

Compound[a]	R′	M.P. °C.	Yield%
1.[b]	H	176	65
2.	2-Me	166-167	69
3.	3-Me	187-188	70
4.	4-Me	185	60
5.	4-OMe	176	60
6.	4-Cl	163-164	65
7.[c]	4-Br	160	70
8.[d]	3-Cl	187	60
9.	2-Cl	152	70
10.[g]	2-OMe	169-170	75
11.[e]	$4-CO_2Me$	160-161	65
12.[f]	$4-CO_2Et$	150-152	45
13.	4-F	157-158	55
14.	4-Ph	178	60
15.	$4-CO_2H$	207-208	65

a. Satisfactory nitrogen analyses were obtained for all the compounds.

I.R. (μ) : b. 3.10 (NH) ; c. 3.10 (NH) ; d. 3.12 (NH) ; e. 3.15 (NH), 5.85 (C=O) ; f. 2.99 (NH), 5 81 (C=O).

N.M.R. (δ) : g. 2.33 (2 Me), 3.73 (OMe), 5.36 (-CH_2- and NH), 6.66 (Ar-H at 3′, 4′, 5′, 6′), 7.16 (2-H), 7.4-7.9 (tow protons at 4 and 7).

Compounds 1, 12, 15 were prepared by method B, others by method A.

All the compounds were screened for their inhibitory effect against four organisms : *Staphylococcus aureus, Escherichia coli, Salmonella typhi* and *Bacillus megaterium* by agar diffusion technique[2]. Compounds 2 and 13 showed moderate inhibition against *B. megaterium*. 1 and 9 were active against *E. coli*. Other compounds were devoid of any activity.

Experimental

Melting points were taken in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 Spectrophotometer in KBr. N.M.R. spectrum was recorded on a Varian A-60-D Spectrometer in $CDCl_3$ using TMS as an internal standard.

1-Hydroxymethyl-5,6-dimethylbenzimidazole (I) — 5,6-Dimethylbenzimidazole (2.19 g.) was suspended in 25 ml of boiling water. Formalin (2 ml) was added to it in small portions with stirring. The reaction mixture after being stirred for 15 min. was left overnight. The solid product thus obtained was filtered, washed with water and recrystallised from ethanol, yield 75°/₀ ; m.p. 197-198° ; m. m. p. with 5, 6-dimethylbenzimidazole 170-190° ; i.r. : 3.25μ (Found : N, 15.83°/₀. Calcd. for $C_{10}H_{12}N_2O$; N, 15.90°/₀).

1-Acetoxymethyl-5, 6-dimethylbenzimidazole (II)— I (1.0g.) and acetic anhydride (5 ml) were heated under reflux for 30 min. The contents were poured in 100 ml of cold water with stirring. The solid mass was filtered, washed with water and recrystallised from ethanol ; yield 65°/₀ ; m.p. 225° ; i.r. : 6.00μ(C=O) ; (Found : N, 12.92°/₀. Calcd. for $C_{12}H_{14}N_2O_2$; N, 12.83°/₀).

1-(4-Nitrobenzoyloxymethyl)-5, 6-dimethylbenzimidazole (III)— Freshly prepared 4-nitrobenzoyl chloride (1.0 g.) dissolved in 25 ml of dry benzene was treated with 0.80 g. of I. The reaction mixture was refluxed for 2 hr under anhydrous conditions. After removing benzene by distillation the solid mass was triturated with 10°/₀ sodium carbonate solution. It was then washed with water and recrystallised (ethanol) ; yield 60°/₀ ; m. p. 176° ; i. r. : 5.78μ (C=O), 6.49, 7.41μ(NO_2) (Found N,12.46. Calcd. for $C_{17}H_{15}N_3O_4$, N, 12.91°/₀).

1-Arylaminomethyl-5,6-dimethylbenzimidazole(IV)– Method A : To a hot solution of 5,6-dimethylbenzimidazole (1.46 g. ; 0.01 mole) in 15 ml of ethanol, 1.5 ml of formalin and an appropriate amine (0.01 mole) were added. The reaction mixture was stirred for 15 min. and then allowed to stand at room temp. overnight. The crude IV thus obtained was purified to analytical purity from ethanol.

Method B : A suitable aromatic amine (0.01 mole) and I (1.76 g. ; 0.01 mole) were heated in 15 ml of ethanol for 30 min. After cooling the product was filtered and recrystallised from ethanol. Various IV thus synthesised are listed in Table 1 along with their physical data.

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Spectrophotometric Studies on Some Hydroxy Azocompounds in Organic Solvents of Varying Polarities and in Buffer Solutions.

A. M. HAMMAM, I. M. ISSA, S. A. AMIN and H. DISSOKI

Chemistry Department, Assiut University, Assiut, Egypt.

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The uv and visible spectra of some hydroxy azocompounds of increasing fused benzene rings are investigated in organic solvents of varying polarities in relation to molecular structure and polarity of the medium. The spectra are studied in aqueous buffer solutions and in buffer solutions containing 30% dioxane. The variation of absorbance with pH is utilised for the determination of pK values of the compounds. The effects of substituent λ_{max} and pK are also studied.

THE absorption spectra of azobenzene and its derivatives have been the subject of some investigations[1-13], the bands observed were shown to be due to $\pi-\pi^*$ and $n-\pi^*$ transitions[1]. The weak $n-\pi^*$ transitions of azobenzene in acid medium were assigned to separate n_a and n_p levels of the two n_s electrons.

Toku Vyemura[9] found that absorption bands in the spectra of hydroxy azocompounds are generally red shifted with increasing *p*H. Ufimtsev[13] showed that the insolubility of azocompounds, e.g. 1-phenyl-azo-2-naphthol in alkalies is due to their limited solubility in water.

The present work deals with the spectrophotometric studies of some hydroxy azobenzenes and their SO_3H derivatives containing fused benzene rings in organic solvents of varying polarities, in aqueous solutions and aqueous solutions containing 30% dioxane. It is attempted to clarify the effect of molecular structure on the spectral behaviour of the compounds.

Experimental

Azo compounds were prepared according to the method of Kamel[14]. The structure of the compounds studied is shown in Table 1. 10^{-4} *M* stock solutions were prepared by dissolving the accurate weight of the compound in the appropriate volume of the required solvent. For measurements in buffer solutions, due to low solubility of the compounds in water and alkali[11], freshly prepared solutions were obtained by dissolving the compound in 30% dioxane. The sulphonated derivatives were dissolved in redistilled water.

The universal buffer solutions of *p*H 2-12 were prepared as reported by Britton[15]. The *p*H's of the solutions were checked using a radiometer *p*H meter model 28 accurate to ± 0.05 units.

The absorption spectra in the uv and visible regions were recorded on a Zeiss spectrophotometer using 1.0 cm matched silica cells.

The compounds investigated are 1-hydroxy-2-phenyl azo-naphthalene(I), 2-hydroxy-1-phenyl azo naphthalene(II), 9-hydroxy-10-phenyl azo acenaphthene(III), 5-hydroxy-6-phenyl azo chrysene(IV) and 6-hydroxy-5-phenyl azo chrysene and their para sulphonated derivatives.

Results and Discussion

I–Spectra in Organic Solvents :

It is clear from the spectra of the compounds investigated (Table 1, Fig. 1) that both λ_{max} and ϵ_{max} of the absorption bands are readily influenced by the nature of the solvent. The electronic absorption spectra of the compounds are composed of two sets of bands. The uv bands correspond to the $\pi-\pi^*$ transition within the aromatic system. The other bands appearing in the visible region may be ascribed to the excitation of the π-electrons of the azo group influenced by charge

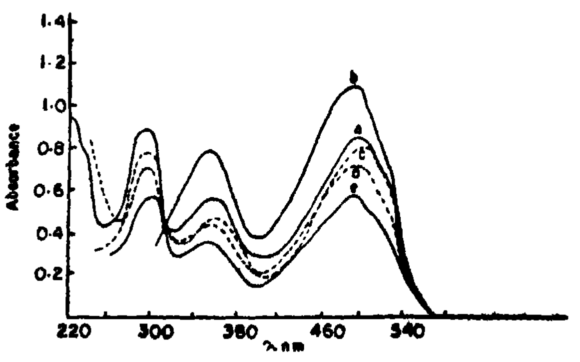


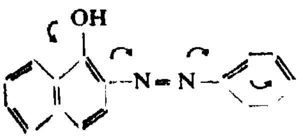
Fig. 1. Absorption spectra of $4\times10^{-5}M$ I in different organic solvents. a—Ethyl alcohol, b—ether, c—chloroform, d—Dioxane, e—Carbon tetrachloride.

TABLE 1—λ_{max} AND ϵ_{max} FOR SOME AZOCOMPOUND IN ORGANIC SOLVENTS

Compound No.	Ethyl alc.		Ether		$CHCl_3$		Dioxane		CCl_4	
	λ_{max}	$\epsilon\times10^{-3}$	λ_{max}	$\epsilon\times10^{-3}$	λ_{max}	$\epsilon\times10^{-3}$	λ_{max}	$\epsilon\times10^{-3}$	λ_{max}	$\epsilon\times10^{-3}$
I	230	21.5								
	256									
	312	8.5	320	S	315	4.25	310	8.0	315	10.0
	480	17.5	465	9.25	480	9.75	470	19.0	470	21.2
II	293	22.50			295	19.75			300	S
	360	14.50	350	20.0	360	12.00	355	11.25	355	6.75
	494	21.75	490	28.0	496	20.75	493	18.25	493	11.0
III	210	38.0								
	255	38.25								
	265	40.0					265	34.5		
	290	19.5	390	6.5			290	15.5	290	23.0
	480	30.5	470	22.75			480	24.0	475	24.5
IV	235	38.75					255	27.5		
	250	44.0			285	31.8	290	S	290	S
	335	5.75	340	6.75	340	7.5	340	6.5	340	4.0
	485	26.0	480	29.75	490	29.8	485	24.5	480	15.2
	505	S	500	30.75	510	30.0	510	25.0	510	15.5
V	225	22.75								
	270	34.0			275	S	270	33.0	275	S
	330	10.25	330	9.5	335	15.25	334	10.75	335	13.5
	395	5.75	400	S	405	S	395	S	405	S
	505	10.0	495	9.0	504	14.5	502	10.75	500	12.5

S = Shoulder

transfer originating from the OH-group and sinking in the phenyl ring, which can be represented as follows :

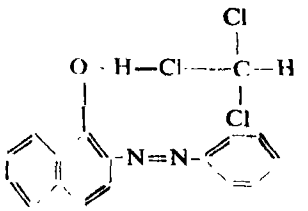


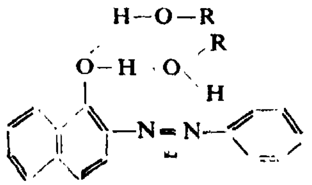
The effect of the polarity of the medium :

In general, the increase of the polarity of the medium, shifts the bands to higher wavelengths, i.e. in the order *ethyl alcohol > ether > $CHCl_3$ > CCl_4*, which shows that these bands are of the $\pi-\pi^*$ transition type[16].

1. The uv bands located near 312 nm in case of compound I or near 335 nm in the case of compounds IV and V, are blue shifted in ethanol relative to ether, although ethyl alcohol (26 D) is a solvent with relatively high polarity compared to ether (4.335 D). The blue shift in this $n-\pi^*$ transition band in alcohol relative to ether, results from H-bonding (the lone pair of electrons on azo nitrogen acts as an electron donor to the hydrogen of the solvent, which lowers the energy of n-orbital, and hence a blue shift in alcohol relative to ether.

2. The visible band (C.T. band) is slightly red shifted in alcohol relative to other solvents such as ether, CCl_4 and dioxane. This small red shift can be explained on the basis that the alcohol molecules associate with the OH-group through H-bond formation. This can readily occur through either the oxygen or hydrogen of the OH-group as follows :





(Compound I)

Such association leaves a negative charge on oxygen of the OH-group which in turn causes more delocalisation of electrons, i.e. requires lower energy and hence a red shift is observed in alcohol.

3. It is also worthy to mention that the C. T. band suffers a slight red shift in $CHCl_3$ (5.05 D) relative to ethyl alcohol. This may be due to the strong intermolecular hydrogen bond formed between the highly negative Cl-atom and the H-atom of the OH-group. However, the red shift of the visible band in alcohol or $CHCl_3$ supports the C. T. nature of this band.

The effect of molecular structure :

It is clear from Table 1, Fig. 2 that the increase in the number of fused benzene rings in the compounds investigated causes a red shift in the position of λ_{max} of the bands. This behaviour may be due to increasing conjugation through the whole molecule with increasing the number of benzene rings, i.e. more delocalisation of the n-electrons which in turn facilitates the excitation of the these electrons and hence require lower energy and a red shift is attained.

II-Spectra in Buffer Solutions :

The visible absorption spectra of some of the compounds (nonsulphonated) investigated have been carried out in universal buffer solutions containing 30% dioxane in order to overcome the low solubility of these compounds in pure aqueous medium or dilute alkali[12]. The *p*K values obtained for these compounds and their *p*-sulphonated derivatives are depicted in Table 2. The spectra of compounds I, II and their *p*-sulphonated derivatives and *p*-SO_3H of compound III in aqueous buffers or containing 30% dioxane in solutions of low *p*H are characterised by an absorption band with λ_{max} located in the wavelength range 470 – 510 nm. This band is comparable to those observed in organic solvents and is mainly due to absorption by species with nonionised OH-group. On increasing the *p*H of the medium, the band becomes broad and exhibits a red shift as a result of the partial ionisation of the OH-group (cf. Fig. 3). This behaviour is due to the strong intramolecular H-bond formed between the ortho-OH group and the lone pair of electrons of the azo group[11]. The spectra of these compounds also exhibit an isosbestic point (Fig. 3), denoting the existence of an equilibrium,

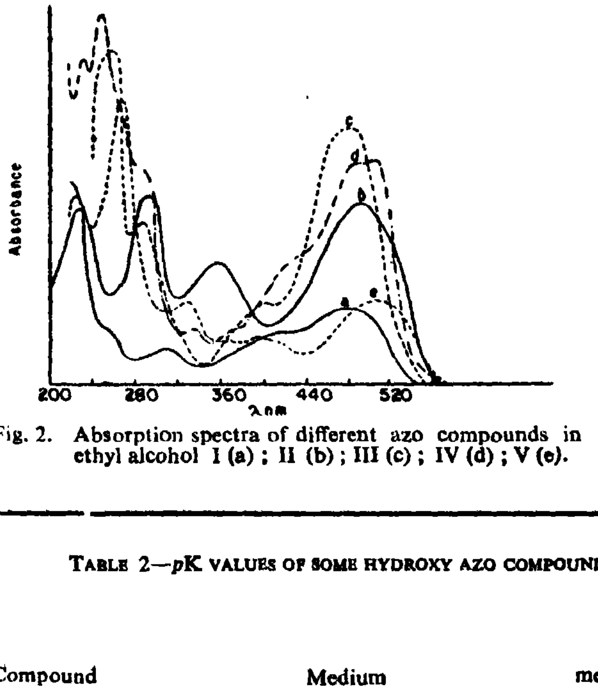


Fig. 2. Absorption spectra of different azo compounds in ethyl alcohol I (a) ; II (b) ; III (c) ; IV (d) ; V (e).

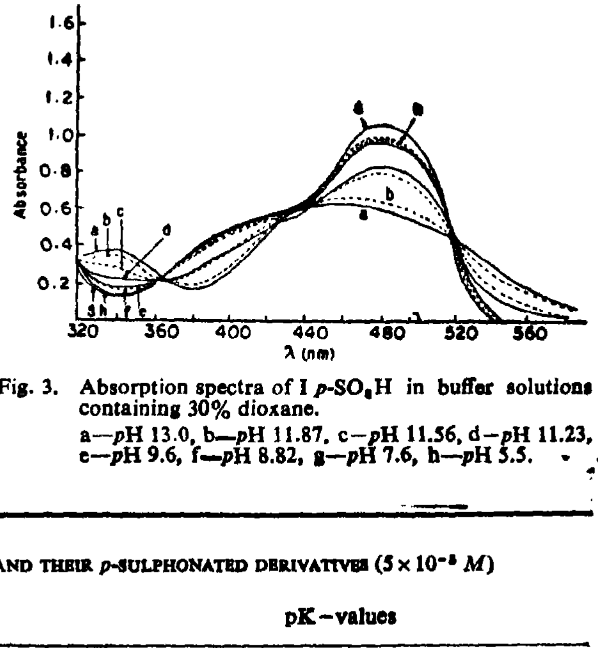


Fig. 3. Absorption spectra of I *p*-SO_3H in buffer solutions containing 30% dioxane.
a—*p*H 13.0, b—*p*H 11.87, c—*p*H 11.56, d—*p*H 11.23, e—*p*H 9.6, f—*p*H 8.82, g—*p*H 7.6, h—*p*H 5.5.

TABLE 2—*p*K VALUES OF SOME HYDROXY AZO COMPOUNDS AND THEIR *p*-SULPHONATED DERIVATIVES (5×10^{-5} *M*)

Compound	Medium	pK-values 1st method	2nd method	3rd method	Mean
I	30% dioxane	11.35	11.40	11.61	11.38
I(*p*-SO_3H)	30% dioxane	11.18	11.18	11.19	11.18
I(*p*-SO_3H)	Aqueous-buffer	11.05	11.06	11.05	11.05
II	30% dioxane	11.25	11.25	11.20	11.25
II(*p*-SO_3H)	30% dioxane	10.35	10.30	10.40	10.35
II(*p*-SO_3H)	Aqueous	9.70	9.60	9.70	9.65
III	30% dioxane	11.30	11.30	11.35	11.30
III(*p*-SO_3H)	30% dioxane	11.15	11.20	11.18	11.20
III(*p*-SO_3H)	Aqueous	11.10	11.10	11.13	11.10

essentially an acid-base between ionised and nonionised forms :

$$HL \rightleftharpoons L^- + H^+$$

III—Determination of pK :

The variation of absorbance with pH is utilised for the determination of the acid dissociation constants of the compounds. For this purpose three different methods are applied :

i—*Half-wave Height*[17] : This method depends on the principle that pK is equal to the value of pH at which the two equilibrium species exist in equivalent quantities, i.e. at half-length of the A-pH curve.

$$pK = pH \text{ at } A_{\frac{1}{2}}$$

$$A_{\frac{1}{2}} = \left(\frac{A_{max} - A_{min}}{2}\right) + A_{min} \qquad ...(1)$$

where A_{max} and A_{min} are the maximum and minimum absorbances on the A-pH curve.

ii—*The limiting absorbance method*[17] : This method makes use of the following relation :

$$pH = pK + \log\left(\frac{A}{A_{max} - A}\right) + \log \bar{v}$$

The pK values determined by this method are low in some cases due to partial overlap of absorption bands leading to high background. This does not allow attainment of a low A_{min} value on the A-pH curve. The error due to interference of the different species can be eliminated by using the following relation[18].

$$pH = pK + \log \bar{v} + \log \frac{A_2 - A_1}{A_3' - A_2'},$$

in which A_1 and A_3 are the absorbances in media containing either HL or L^- species only, A_2 and A_2' the absorbances in solutions where HL and L^- coexist.

iii—*The modified Collecter method*[19], as applied for the determination of the dissociation constants of weak acids[20], for this method :

$$K = \frac{{}^{C}H_1^+ - {}^{C}H_2^+}{M - 1}$$

where

$$M = \left(\frac{A_2 - A_1}{A_3 - A_2}\right)\left(\frac{{}^{C}H_1^+ - {}^{C}H_2^+}{{}^{C}H_2^+ - {}^{C}H_3^+}\right)$$

A_1, A_2 and A_3 are the absorbances at ${}^{C}H_1^+$, ${}^{C}H_2^+$ and ${}^{C}H_3^+$ respectively. The pK values obtained are shown in Table 2.

It is obvious that the pK values for the p-sulphonated derivatives are lower than those for the nonsulphonated compounds. This can be ascribed to the -M effect of the sulphonic group which leads to a weakening of the intramolecular H-bond. This latter causes in turn easier liberation of the proton of the OH-group and hence lower pK values.

For compounds IV, V and their p-sulphonated derivatives, the spectra are very little influenced by increasing the pH of the medium and hence the dissociation constants of these compounds are difficult to obtain.

From Table 2, it is obvious that in case of I and its sulphonic derivative, the difference between their pK-values is lower than between II and its sulphonic derivative. This is probably due to decreased H-bonding in compound II which lowers the ionisation than in compound I.

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Synthesis and Application of Oxazolophenothiazines

M. A. ABBADY*, A. M. OSMAN and A. A. EL-BAHNASAWY

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt, A.R.E.

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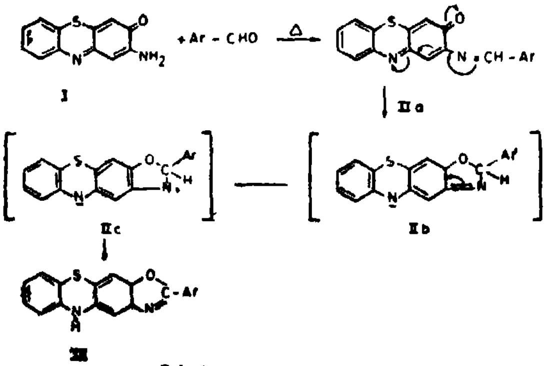
2-Aryl-5*H*-oxazolo [4, 5-*b*] phenothiazines (III) were synthesized by interaction of 3-aminophenothiaz-2-one (I) with the appropriate aromatic aldehydes in the presence of a basic catalyst or by its fusion with aromatic aldehydes. Interaction of (I) with benzyl chloride gave 2-aryl-5-benzyloxazolo [4, 5-*b*] phenothiazines (IX) which alternatively were obtained by direct interaction of (I) with benzyl chloride.

5*H*-oxazolo [4, 5-*b*] phenothiazine (VI) and 2-methyl-5-acetyloxazolo [4, 5-*b*] phenothiazine (VII) were also prepared. 2-(*p*-aminophenyl) oxazolo [4, 5-*b*] phenothiazine was utilized for the preparation of azoic dyes.

Some of (III) and (IX) showed remarkable biological activities.

OXAZOLOPHENOTHIAZINES, as a new poly-condensed diheterocyclic compounds, may be of considerable importance as reagents in biological assays or in the fields of dyes, optical brightness and photographic sensitizers. The starting material for preparing these compounds is 3-amino-phenothiaz-2-one (I) which was prepared according to a simple method of Abbady and Osman[1].

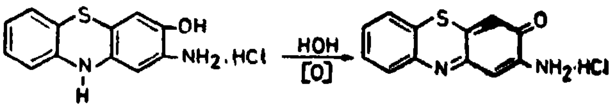
Condensation of (I) with aromatic aldehydes under various conditions gave fine crystals of oxazolophenothiazines(III). This condensation was carried out by refluxing the reactants in the presence of a basic catalyst. In certain cases the reaction could be promoted by the addition of few drops of alcoholic ferric chloride. The same reaction could be conducted by fusion of the reactants although the yields of (III) are much lower. The reaction is expected to proceed as follows[2] :



Scheme a

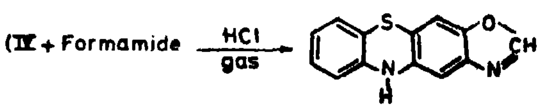
The higher yields of oxazolophenothiazines (III) by solvent method can be attributed to the fact that the protropic shift of the hydrogen ion in (II)c is relatively easier due to the effect of basic catalyst. Oxazolophenothazines are yellow to brown compounds with varying degree of fluorescence in organic solvents and with high melting points (Table 1). These compounds are quite stable in alkaline solutions and cold dilute mineral acids.

However, when boiled with conc. hydrochloric acid, they are cleaved to form 3-amino-2-hydroxyphenothiazine hydrochloride (IV) (which is readily oxidized by atmospheric oxygen to the 3-amino-phenothiaz-2-one hydrochloride[1](V)) and the original aldehyde.



(IV) (V)

The parent oxazolophenothiazine, namely 5*H*-oxazolo [4,5-*b*] phenothiazine (VI) was prepared by heating (IV) 2-hydroxy-3-amino-phenothiazine hydrochloride (*in situ*) with formamide in the presence of hydrogen chloride as a catalyst[3]. The structure of this compound was confirmed by analytical values and spectroscopic data besides its general characteristics.



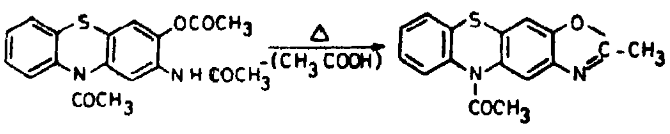
(VI)

2-methyl-5-acetyloxazolo [4,5-*b*] phenothiazine(VII) was prepared by heating the triacetate(VIII) at 195°.

*For correspondence

This is apparently accomplished by elimination of the elements of acetic acid molecule[4]. I.R. absorption spectrum of this compound showed characteristic bands at 1680 cm^{-1} (N-acetyl), 1190, 1160 cm^{-1} for the cyclic -C-O-C- group and at 1580 cm^{-1} for C=N. This compound exhibits a magenta colour in concentrated sulphuric acid.

Unlike to (III) the N-benzylderivatives (IX) are unaffected by concentrated hydrochloric acid, this demonstrates clearly the effect of substituents on the stability of the oxazole ring. I.R.[5] absorption spectra of (IX) indicated the absence of the band at 3340 cm^{-1}, characteristic for a secondary amino group. These compounds are yellow to cream in colour with melting



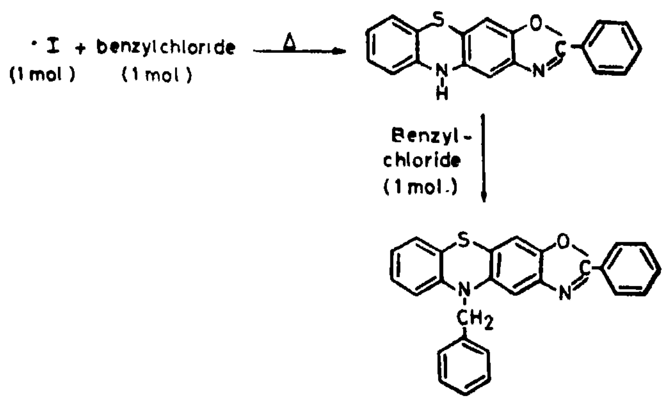
(VIII) (VII)

Interaction of the aminophenothiazine with benzyl chloride : This reaction gave different products according to the amount of benzyl chloride used. Thus with equimolecular amounts of (I) and benzyl chloride, the resulting product was identified as 2-phenyloxazolo [4,5-*b*] phenothiazine(III, Ar= phenyl), whereby, with two moles of benzyl chloride the product was 2-phenyl-5-benzyloxazolo [4, 5-*b*] phenothiazine (IX, Ar= phenyl).

Transformation of the former to the latter was easily effected by heating with benzyl chloride thus confirming the route of the reaction, (Scheme b).

points lower than the corresponding oxazolophenothiazines and exhibited an intense violet to green fluorescence in concentrated sulphuric acid.

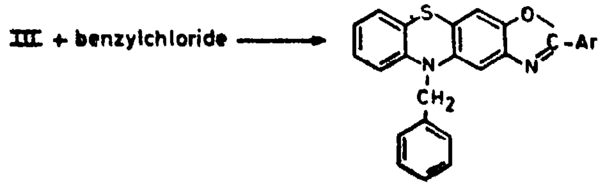
The above described oxazolophenothiazines are considered to be suitable compounds for the preparation of heterocyclic dyes. Accordingly 2-(*p*-nitrophenyl) oxazolo [4,5-*b*] phenothiazine was reduced[6] to the corresponding amino compound, which could only be diazotized by nitrosylsulphuric acid and the resulting diazonium salt was coupled with various components to give some interesting azoic dyes, which could be used for dyeing cotton and wool or synthetic fibres according



(IX) Ar = -C_6H_5

Scheme b

Other N-benzyloxazolophenothiazines were prepared by the action of benzyl chloride on different 2-aryloxazolophenothiazines. It must be mentioned that this reaction proceeds smoothly if the aryl group of (III) contains electron withdrawing group.



(IX)

to the type of the coupler. These dyes showed good substantivity and fastness properties[7].

Some of the hitherto synthesized oxazolophenothiazines (III), and (IX) were tested *in vitro* for their biological activities on some bacteria like *Staphylococcus aureus*, *Sarcina lutea* and *Bacillus subtilis*.

Remarkable effects were obtained at concentrations of 1 x 10^{-1} to 1 x 10^{-5} *M*. The N-substituted oxazolophenothiazines (IX) showed superior biological activity than the corresponding oxazolophenothiazines in all experiments.

On the other hand the role of substituent in (III) or (IX) is of no considerable value in this connection and the main effect is attributed to the thiazine nucleus. Concentration at $10^{-8} M$ gave 100% inhibition in case of 2-(*p*-nitrophenyl) oxazolophenothiazine and the corresponding 5-benzyl derivative in all tests.

Experimental

Melting points taken on a Mel-Temp. electrically heated, melting point unit and are uncorrected. The Infrared absorption spectra were determined with a Unicam SP 200 G spectrophotometer using KBr wafer technique. The uv spectra were recorded on a Unicam SP 8000 ultraviolet recording spectrophotometer using 1 cm. matched cells and spectrally pure solvents.

3-aminophenothiaz-2-one (I) : This was prepared according to the method of Abbady and Osman[1].

2-Aryl-5H-Oxazolo [4,5-b] phenothiazines (III) :

(i) Fusion method :

The aminophenothiazone (1 mol) was covered with the aromatic aldehyde (2 mol) and refluxed in an oil bath for thirty minutes but in the case of nitroaldehyde the mixture was heated in the direct flame for three minutes only. The reaction mixture was cooled, triturated with few ml of alcohol, the solid product was collected and washed several times with ethyl alcohol, then recrystallized from the proper solvent.

(ii) Solvent method :

Aminophenothiazone (0.01 mol) and aromatic aldehyde (0.01 mol) were refluxed for 4 hours in n-butanol (20 ml) in the presence of dry piperidine (0.002 mol). The reaction mixture was cooled and the resulting product was collected, washed with dilute alcohol, then crystallized from the proper solvent. In the case of liquid aromatic aldehydes, few drops of alcoholic ferric chloride solution must be added at the end of the reflux to promote the formation of the expected oxazoles. The results are listed in Table 1.

5H-Oxazolo [4,5-b] phenothiazine (VI) : A mixture of (I), (0.01 mol), zinc dust (3 g.) and conc. HCl (10 ml) was refluxed for 20 min., the mixture was filtered rapidly, formamide (0.03 mol) was added to the filtrate. This mixture was refluxed for 20 min. in the presence of hydrogen chloride gas, the mixture was cooled, then extracted with benzene or light petroleum (80-100°). The extracted substance was collected and recrystallized from ethanol into pale green needles, m.p. 210°. Anal. Calcd. for : $C_{13}H_8N_2OS$: C, 65.00 ; H,3.33 ; N, 11.66 ; S, 13.13. Found : C, 65.15 ; H, 3.25 ; N, 11.52 ; S, 13.09.

2-Methyl-5-acetyl-oxazolo[4,5-b]phenothiazine(VII):

(i) *Preparation of 3-acetylamino-2-acetoxy-5-N-acetylphenothiazine (VIII)* :

To a colourless mixture of I (1 g.) in 10 ml. glacial acetic acid and zinc dust, 3 ml acetic anhydride was added. The mixture was heated on a water bath for 10 min., filtered, diluted with water to 100 ml. and left in a refrigerator overnight. The precipitated solid was crystallized twice from propyl alcohol. Yield (0.26 g) colourless crystalline material, m.p. 227-228°, soluble in ethanol, sparingly in benzene and ether.

The i.r. absorption spectrum of this molecule shows characteristic bands at 1770 cm^{-1} (aromatic acetate), 1675 cm^{-1} (N-acetyl) and 1720 cm^{-1} (acetylamino). Anal. Calcd. For $C_{18}H_{16}N_2O_4S$: C, 60.66 ; H, 4.42 ; N, 7.86 ; S, 9.00. Found : C, 61.13 ; 61.18 ; H, 3.90 ; 4.05 ; N, 8.06 ; 8.23 ; S, 8.79, 2.81%.

(ii) *Fusion of triacetate (VIII) and preparation of (VII)* : A pure sample of 3-acetylamino-2-acetoxy-5-N-acetyl-phenothiazine (VIII) (4 g) was heated in a porcelain dish at 200° until no more acetic acid was evolved. The deep brown melt was cooled, extracted with ethanol, the extraction mixture was concentrated, cooled, whereby colourless product was precipitated which collected and crystallized from ethanol into colourless needles, m.p. 138-139°. Anal. Calcd. For $C_{16}H_{12}N_2OS$: C, 64.86 ; H, 4.05 ; N, 9.46. Found : C, 64.76 ; H, 4.15 ; N, 9.51.

2-Aryl-5-benzyl-oxazolo[4,5-b] phenothiazines(IX) :

(i) *Reaction of (I) with benzyl chloride and preparation of 2-phenyl-5-benzyl-oxazolo [4,5-b] phenothiazine (III)*, ($Ar=C_6H_5$) :

Aminophenothiazone (1 mol) was covered with benzyl chloride (1 mol) and the mixture was refluxed on the direct flame for about 2 hrs. The reaction mixture was cooled and the deposited solid was collected, washed with few drops of alcohol and crystallized from benzene, m.p. 310° not depressed on admixture with an authentic sample obtained by reaction of (I) with benzaldehyde as previously mentioned and the product was identified as 2-phenyl [4,5-*b*] oxazolophenothiazine (c.f. Table 1).

By refluxing I (1 mol) and benzyl chloride (2 mol) under the above conditions 2-phenyl-5-benzyl-oxazolo [4,5-*b*] phenothiazine was obtained, m.p. 235° (c.f. Table 2).

TABLE 1—ANALYTICAL DATA OF 2-ARYL-5-*H*-OXAZOLO [4, 5-*b*] PHENOTHIAZINES (III).

(III), 2-Ar	M. P. °C	Solvent of crystall-ization	Calculated (%)			Molecular Formula	Found (%)		
			C	H	N		C	H	N
Phenyl	310	B	72.15	3.79	8.86	$C_{19}H_{12}N_2OS$	72.02	3.89	8.65
Cinnamyl	315-317	E	73.68	4.09	8.18	$C_{21}H_{14}N_2OS$	73.59	4.15	7.89
Anisyl	270	B	69.36	4.04	8.08	$C_{20}H_{14}N_2OS$	69.27	4.14	8.10
o chlorophenyl	240	B	65.14	3.14	8 00	$C_{19}H_{11}N_2OSCl$	65.40	3.32	8.19
Salicyl	312	P	68.67	3.61	8.43	$C_{19}H_{12}N_2O_2S$	68.80	3.72	8.13
p-Nitrophenyl	335	Bu	63.33	3.06	11.66	$C_{19}H_{11}N_3O_3S$	63.41	3.21	11.51
o-Nitrophenyl	230	Bu	63.33	3.06	11.66	$C_{19}H_{11}N_3O_3S$	63.25	3 30	11.45
m-Nitrophenyl	298	Bu	63.33	3.06	11.66	$C_{19}H_{11}N_3O_3S$	63.48	3.51	11.30
p-Aminophenyl	291	P	68.67	3.93	12 68	$C_{19}H_{13}N_3OS$	68.61	4.01	12.71
m-Aminophenyl	297	P	68.67	3.93	12.68	$C_{19}H_{13}N_3OS$	68.52	3.75	12.65
o-Aminophenyl	304	P	68.67	3 93	12.68	$C_{19}H_{13}N_3OS$	68.48	3.62	12.49

B benzene ; E, ethanol, Bu, n-butanol, P, petroleum ether (80-100°).

TABLE 2—ANALYTICAL DATA OF 2-ARYL-5-BENZYL-OXAZOLO [4, 5-*b*] PHENOTHIAZINES (IX).

(IX), 2-Ar	M. P. °C	Solvent of crystall-ization	Calculated (%)			Molecular formula	Found (%)		
			C	H	N		C	H	N
Phenyl	235	E	76.84	4.43	6.89	$C_{26}H_{18}N_2SO$	76.72	4.52	7.07
2-phenyl (*o*-benzyloxyphenyl)	240	E	77.34	4.71	5.47	$C_{33}H_{24}N_2SO_2$	77.52	4.90	5.23
p-nitrophenyl	257	B	69.17	3.76	9.31	$C_{26}H_{17}N_3O_3S$	69.37	3.51	8.95
m-nitrophenyl	265	B	69.17	3.76	9.31	$C_{26}H_{17}N_3O_3S$	69.48	3.91	9 42
o-nitrophenyl	262	B	69.17	3.76	9.31	$C_{26}H_{17}N_3O_3S$	69.05	3.65	9.51
Anisyl	260	B	74.31	4.58	6.42	$C_{27}H_{20}N_2O_2S$	74,41	4.25	6.65

E = ethanol, B = benzene.

(ii) *Reaction of 2-aryloxazolophenothiazine with benzyl chloride and preparation of (IX)*: Oxazolophenothiazines III (1 mol) were covered with benzyl chloride (more than 1 mol) and the mixture was refluxed on the direct flame for about 2 hours. The excess benzyl chloride was removed, the reaction mixture was collected and the deposited solid was collected, washed with alcohol and crystallized from the proper solvent. The results are shown in Table 2.

Reduction of 2-nitro-aryloxazolophenothiazines: A finely powdered sample of the nitro-oxazolophenothiazines (0.01 mol) was refluxed for 3 hr. with stannous chloride (0.02 mol) in the presence of alcoholic hydrogen chloride solution (50 ml). The reaction mixture was cooled and the precipitated aminohydrochloride was filtered and dried. The product was suspended in water, then treated with an equivalent amount of sodium carbonate solution. The free amine was collected and crystallized from the proper solvent. The results are shown in Table 1.

Preparation of oxazolophenothiazine dyes:[8]

(i) *Diazotization of 2-(p-aminophenyl) oxazolo [4,5-b] phenothiazine*: Aminophenyloxazolophenothiazine (0.01 mol) was dissolved in glacial acetic acid (5 ml), was cooled at 0°, and then nitrosylsulphuric acid (5 ml, 0.0113 mol $NaNO_2$ in 5ml conc. H_2SO_4) was added very slowly at such a rate that the temperature did not exceed 0°. When all the acid has been added, the mixture was allowed to stand in an ice bath for 30 min. with occasional stirring. The diazonium salt solution was poured onto ice (50 g.) and left to cool.

(ii) *Disperse Dyes*:

Coupling of diazotized p-*aminophenyloxazolophenothiazine with naphthols*: The calculated amount of freshly prepared diazonium salt of aminophenyloxazolophenothiazine was coupled with α- and β-naphthol (0.29 g. dissolved in 20 ml of 1 *N* NaOH solution). The reaction mixture was neutralized by the addition of sodium carbonate, whereas, with α-naphthol a reddish-brown dye was deposited, crystallized from ethanol into brown needles m.p. 280°. Anal. Calcd. For $C_{31}H_{17}N_4O_2S$: C, 73.08 ; H, 3.33 ; N, 11.00 ; Found : C, 72.95 ; H, 3.24 ; N, 11.12%, λ_{max} 495 ϵ_{max} 40125 with β-naphthol a pink dye was deposited and crystallized from methanol as red needles m.p. 249°. Anal. Calcd. for $C_{31}H_{17}N_4O_2S$: C, 73.08 ; H, 3.33 ; N, 11.00. Found : C, 73.21 ; H, 3.42 ; N, 10.92. λ_{max} 480, ϵ_{max} 38210. Other dispersed dyes were obtained by coupling the above diazonium salt according to the normal procedures with naphthylamines and 3-methyl-1-phenyl-5-pyrazolone.

The prepared dyes were applied as disperse dyes on Nylon in acidic solution and showed good substantivity and satisfactory fastness properties.

(iii) *Direct Dyes* :

Coupling with J-acid and o-acid: This was proceeded normally in an alkaline medium to give a water-soluble reddish-violet dyes ; they were precipitated from the coupling mixture by the addition of sodium carbonate, showed satisfactory substantivity for dyeing cellulosic fibres in neutral solution, wool and nylon in acidic solution, with violet colour and sufficient fastness properties.

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Synthesis of Some New Arylazo Derivatives of Thio Pyrimidines

V. K. MAHESH, R. N. GOYAL* and (Mrs.) RAMA GUPTA

Department of Chemistry, University of Roorkee, Roorkee.

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A number of 2-thio analogues of 5-arylazo-pyrimidines have been synthesised by the condensation of 6-methyl-2-thio uracil, 2-methylthio-4-hydroxy-6-methyl pyrimidine and 2-ethylthio-4-hydroxyl-6-methyl pyrimidine with diazotised anilines. The structure of these compounds was further confirmed by I.R. Spectra.

STUDIES have shown that arylazogroups are active in promoting antineoplastic activity.[1,2] Recently, the synthesis of a number of pyrimidine derivatives bearing the arylazo group has been reported from these laboratories.[3] In further quest for novel anticancer drugs, an attempt has been made to synthesise some thio analogues of pyrimidines bearing the arylazo group at position 5.

The compounds described in this communication have been synthesised, by reacting aryl diazonium chlorides with properly substituted pyrimidines. The structure of the compounds have been established by I. R. spectra (all compounds gave a characteristic peak of $-N{=}N-$ bond, at position 5, enolic-OH gp. at position 4 and thiol gp. at position 2). The arylazo group at position 5 was further confirmed by reducing the arylazo derivative with Sn + HCl. In case of 2-methylthio-4-hydroxy-6-methyl-5-phenylazo-pyrimidine, 5-amino-2-methylthio-4-hydroxy - 6 - methyl pyrimidine was obtained.

The reaction of aryl diazonium chloride with pyrimidine was smooth and the coupled products were obtained in good yields. The reactivity followed the expected course, diazonium chlorides with electron with drawing groups in position 2 and 4 gave better yields.

Experimental

6-methyl-2-thiouracil, 2-methylthio-4-hydroxy-6-methyl pyrimidine and 2-ethylthio-4-hydroxy-6 methyl pyrimidine, which were required as a starting material for synthesis, were prepared by the method reported in literature.[4]

* For correspondence.

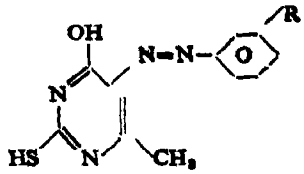
Aniline (0.93 g, 0.01 mol.) was dissolved in dilute hydrochloric acid (10 ml.) and cooled to 0° in an ice bath. Sodium nitrite (0.69 g., 0.01 mol.) was then gradually added. The diazonium salt solution so obtained was filtered into a cold, stirred solution of 6-methyl-2-thio-uracil (1.42 g., 0.01 mol.) in 10 ml. of 10% sodium hydroxide containing 2-3 gms. of sodium acetate. The reaction mixture was held at 0° for 4 hrs. and then left at room temp. for 2 days when a reddish brown solid was separated out. It was filtered, washed well with water and crystallised from ethanol-pyridine mixture and had a m. pt. of 70°.

Analysis: Found : N, 21.8%, calculated for $C_{11}H_9N_4OS$: N, 22.8%.

Other substituted arylazo thio uracils were prepared by the above method starting with substituted anilines. The characteristics of these compounds have been entered in Tables 1-3.

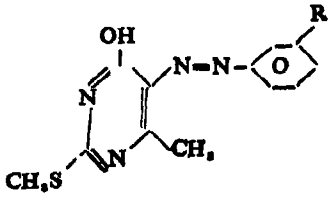
Infra red spectra of these compounds show a band in 1640 – 1590 cm^{-1} region corresponding to $N{=}N$ stretching (Tables 1-3) which confirms the presence of azo bonding. The spectra also show absorption bands in the regions, 2600-2500 cm^{-1} (S-H stretching), 2970-2950 cm^{-1} (C-H stretching due to CH_3), 3600-3500 cm^{-1} and 1400-1300 cm^{-1} (OH group).

TABLE 1—CHARACTERISTICS OF 6-METHYL-2-THIO-5-ARYLAZOURACILS



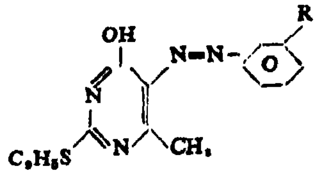
No.	R	M.P. °C	Colour	Formula	I. R. Frequency -N=N-cm
1.	H	70	B	$C_{10}H_{10}SON_4$	1590
2.	2-CH_3	182	B	$C_{12}H_{12}SON_4$	1600
3.	3-CH_3	80	B	$C_{12}H_{12}SON_4$	1590
4.	4-CH_3	168	YB	$C_{12}H_{12}SON_4$	1620
5.	2-OCH_3	155	B	$C_{12}H_{12}SO_2N_4$	1600
6.	3-OCH_3	280	YB	$C_{12}H_{12}SO_2N_4$	1600
7.	4-OCH_3	225	B	$C_{12}H_{12}SO_2N_4$	1640
8.	4-Br	71	Y	$C_{11}H_9SON_4Br$	1630
9.	4-I	220 d	OY	$C_{11}H_9SON_4I$	1630
10.	2-NO_2	224	Y	$C_{11}H_9SO_3N_5$	1590
11.	3-NO_2	215	Y	$C_{11}H_9SO_3N_5$	1600
12.	4-NO_2	225	O	$C_{11}H_9SO_3N_5$	1630
13.	2-Cl	285	Y	$C_{11}H_9SO_2N_4Cl$	1600
14.	3-Cl	95	Y	$C_{11}H_9SO_2N_4Cl$	1595
15.	4-Cl	164	B	$C_{11}H_9SO_2N_4Cl$	1610

TABLE 2—CHARACTERISTICS OF 2-METHYLTHIO-4-HYDROXY-6-METHYL-5-ARYLAZOPYRIMIDINES



No.	R	M.P. °C	Colour	Formula	I. R. frequency cm^{-1}
1.	R	82	YG	$C_{12}H_{12}SON_4$	1600
2.	2-CH_3	105	B	$C_{13}H_{14}SON_4$	1600
3.	3-CH_3	73	B	$C_{13}H_{14}SON_4$	1610
4.	4-CH_3	108	B	$C_{13}H_{14}SON_4$	1630
5.	2-OCH_3	250	O	$C_{13}H_{14}SO_2N_4$	1590
6.	3-OCH_3	75	B	$C_{13}H_{14}SO_2N_4$	1620
7.	4-OCH_3	75	B	$C_{13}H_{14}SO_2N_4$	1600
8.	2-Cl	265	B	$C_{12}H_{11}SON_4Cl$	1620
9.	3-Cl	270	Y	$C_{12}H_{11}SON_4Cl$	1630
10.	4-Cl	160	B	$C_{12}H_{11}SON_4Cl$	1640
11.	4-Br	210	B	$C_{11}H_{11}SON_4Br$	1630
12.	4-F	78	B	$C_{12}H_{11}SON_4F$	1630
13.	2 . 6 Dichloro	105	B	$C_{12}H_{10}SON_4Cl_2$	1600

TABLE 3—CHARACTERISTICS OF 2-ETHYLTHIO-4-HYDROXY-6-METHYL 5-ARYLAZOPYRIMIDINES



No.	R	M.P. °C	Colour	Formula	I. R. Frequency
1.	H	98	B	$C_{12}H_{12}ON_4$	1600
2.	2-CH_3	100	B	$C_{13}H_{14}ON_4$	1600
3.	3-CH_3	95	B	$C_{13}H_{14}ON_4$	1610
4.	4-CH_3	91	B	$C_{13}H_{14}ON_4$	1640
5.	2-OCH_3	75	B	$C_{13}H_{14}O_2N_4$	1610
6.	3-OCH_3	110	B	$C_{13}H_{14}O_2N_4$	1600
7.	4-OCH_3	230	Y	$C_{13}H_{14}O_2N_4$	1630
8.	2-Cl	110	B	$C_{12}H_{11}ON_4Cl$	1610
9.	3-Cl	112	Y	$C_{12}H_{11}ON_4Cl$	1620
10.	4-Cl	102	Y	$C_{12}H_{11}ON_4Cl$	1640
11.	4-I	158	Y	$C_{12}H_{11}ON_4I$	1630
12.	4-F	114	B	$C_{12}H_{11}ON_4F$	1630
13.	2-NO_2	125	Y	$C_{12}H_{11}O_3N_5$	1590
14.	3-NO_2	220	Y	$C_{12}H_{11}O_3N_5$	1600
15.	4-NO_2	210	Y	$C_{12}H_{11}O_3N_5$	1620
16.	2 : 6 Dichloro	225	Y	$C_{12}H_{10}ON_4Cl_2$	1610

B=Brown, Y=Yellow, O=Orange, G=Green.

All melting points are uncorrected and were determined by using a Kofler hot stage apparatus.

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Synthesis of S-(4-Aryl-4H-1,2,4-Triazol-3yl) 2-Mercaptomethyl Benzimidazoles*

K. F. MODI, N. KRISHNAKUMAR, H. J. MEHTA, A. C. PADHYA and S. SOMASEKHARA

Sarabhai Research Centre, Wadi Wadi, Baroda-390007

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A number of benzimidazole derivatives were synthesised from 4-aryl-4H-1,2,4-triazolyl-3-mercaptoacetic acids by condensing with *o*-phenylenediamine and 4-chloro-*o*-phenylene diamine in presence of 4*N* hydrochloric acid. The 4-aryl-4H-1,2,4-triazole-3-thiols, S-(4-aryl-4H-1,2,4-triazol-3yl) mercaptoacetic acids and S-(4-aryl-4H-1,2,4-triazol-3yl) 2-mercaptomethyl benzimidazoles have been screened for antibacterial, antituberculous and antifungal activities. Among them some of the acids showed weak antifungal activity against *Trichophyton mentagrophytes* at 50 mcg/ml concentration.

BENZIMIDAZOLE and its derivatives are known for their fungicidal, antibacterial and anthelmintic activities[1-3]. Moreover 4H-1,2,4-triazole derivatives have been reported as antimicrobial agents[4,5]. So, it has been proposed to synthesise the benzimidazole derivatives containing 4-aryl-4H-1,2,4-triazolyl moiety at 2-position. In this communication S-(4-aryl-4H-1,2,4-triazol-3yl) 2-mercaptomethyl benzimidazoles have been prepared by the following sequence of reactions. All these compounds have been screened for antibacterial, antituberculous and antifungal activities. Among them some of the acids showed weak antifungal activity against *Trichophyton mentagrophytes.*

1. 4-Arylthiosemicarbazides were cyclised with ethylformate in presence of sodium methoxide to get 3-mercapto-4-aryl-4H-1,2,4-triazoles (I).

2. The mercapto triazoles (I) were reacted with monochloroacetic acid to get S-(4-aryl-4H-1,2,4-triazol-3yl) mercaptoacetic acids (II).

3. The 3-thioacetic acids (II) were condensed with *o*-phenylenediamine and 4-chloro-*o*-phenylenediamine to get the title compounds.

Biological data

The *in vitro* antibacterial, antituberculous and antifungal activities were studied by the serial dilution technique[6]. As the compounds are insoluble in broth, they were dissolved in dimethylformamide (DMF) and dilutions were made such that in no instance there was more than 1% DMF in the medium under study. It was confirmed that DMF at such concentrations had no inhibitory effect on the organisms under test. For antibacterial screening, the inoculated broth tubes were incubated at 37° for 24 hours and the dilution inhibiting the growth was noted. For antifungal screening, the inoculated broth tubes were incubated at 28° and the state of growth was observed for 96 hours and the dilution showing no visible growth was noted. Antituberculous tests were carried out in Lownstien-Jenson media. Results were recorded after three weeks' incubation at 37° when tested at 50 mcg/ml concentration. These derivatives showed no inhibitory properties against the organisms.

Experimental

1. *Preparation of 4-Aryl-3-mercapto-4H-1,2,4-triazoles :*

Prepared by the method described earlier[7].

4-Arylthiosemicarbazides (1 mol) and ethyl formate (1 mol) were added to sodium methoxide (1 mol) in absolute methanol, the mixture was refluxed for 8 hours; the solvent was removed and the residue was taken in water and acidified with acetic acid to precipitate 3-mercapto-4-aryl-4H-1,2,4-triazoles. The compounds were crystallised from aqueous alcohol in 68-70% yield.

2. *Preparation of S-(4-Aryl-4H-1,2,4-triazol-3yl) mercaptoacetic acids :*

Prepared by the method described earlier[8].

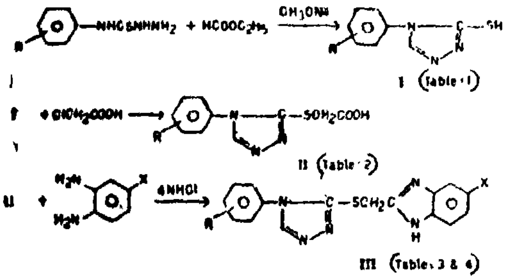
3-Mercapto-4-aryl-4H-1,2,4-triazoles (0.15 mol) were added to monochloroacetic acid (0.207 mol) in 104 ml sodium carbonate (0.414 mol) solution ; the mixture was refluxed for 4-5 hours. The reaction mixture was cooled and acidified with hydrochloric acid to precipitate acids. The compounds were crystallised from hot water.

3. *Preparation of S-(4-Aryl-4H-1,2,4-triazol-3yl) 2-mercaptomethyl benzimidazoles :*

Prepared by the method described earlier[9].

*Presented at 26th Indian Pharmaceutical Congress, Dec. 28-30, 1974, Madras.

S-(4-Aryl-4H-1,2,4-triazol-3yl) mercaptoacetic acids (0.03 mol) and *o*-phenylene diamine (0.02 mol) in 20 ml of 4*N* hydrochloric acid were refluxed for 8 hours. The reaction mixture was cooled and filtered; the filtrate was rendered alkaline with ammonia to obtain S-(4-aryl 4H-1,2,4-triazol-3yl) 2-mercaptomethyl benzimidazoles. They were crystallised from aqueous acetic acid.



R = H, 2-, 3-, 4-CH₃, 2-, 3-, 4-OCH₃, 2-, 3-, 4-Cl, 4-Br & I, 3-CF₃, 2,4-(CH₃)₂, 2-CH₃-4-Cl, 2-CH₃-5-Cl.

X = H, Cl.

The compounds synthesised are listed in Tables 1-4.

TABLE 1—4-ARYL-3-MERCAPTO-4H-1,2,4-TRIAZOLE

S. No.	R	M.P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	3-CH₃	166-70	$C_9H_9N_3S$	21.2	21.9
2.	2-OCH₃	188-90	$C_9H_9N_3OS$	19.9	20.2
3.	3-OCH₃	146-48	$C_9H_9N_3OS$	19.8	20.2
4.	2-Cl	190-92	$C_8H_6ClN_3S$	20.1	19.8
5.	3-Cl	178-80	$C_8H_6ClN_3S$	20.8	19.8
6.	3-CF₃	176-78	$C_9H_6F_3N_3S$	17.7	17.5
7.	4-Br	224-25	$C_8H_6BrN_3S$	16.9	16.4
8.	4-I	199-01	$C_8H_6IN_3S$	13.4	13.8
9.	2,4-(CH₃)₂	204-06	$C_{10}H_{11}N_3S$	20.6	20.4
10.	2-CH₃-4-Cl	198-99	$C_9H_8ClN_3S$	18.4	18.6
11.	2-CH₃-5-Cl	176-80	$C_9H_8ClN_3S$	19.1	18.7

* All the melting points are uncorrected.

TABLE 2—S-(4-ARYL-4H-1,2,4-TRIAZOL-3YL) MERCAPTOACETIC ACID

S. No.	R	M.P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	H	208-09	$C_{10}H_9N_3O_2S$	17.6	17.8
2.	2-CH₃	165-69	$C_{11}H_{11}N_3O_2S$	17.5	16.8
3.	3-CH₃	176-78	$C_{11}H_{11}N_3O_2S$	17.5	16.8
4.	4-CH₃	204-09	$C_{11}H_{11}N_3O_2S$	16.7	16.8
5.	2-OCH₃	190-95	$C_{11}H_{11}N_3O_3S$	15.4	15.8
6.	3-OCH₃	178-80	$C_{11}H_{11}N_3O_3S$	15.5	15.8
7.	4-OCH₃	230-32	$C_{11}H_{11}N_3O_3S$	16.1	15.8
8.	2-Cl	160-62	$C_{10}H_8ClN_3O_2S$	15.6	15.5
9.	3-Cl	178-80	$C_{10}H_8ClN_3O_2S$	15.5	15.5
10.	4-Cl	230-32	$C_{10}H_8ClN_3O_2S$	15.7	15.5
11.	3-CF₃	209-11	$C_{11}H_8F_3N_3O_2S$	14.1	14.1
12.	4-Br	241-43	$C_{10}H_8BrN_3O_2S$	13.4	13.7
13.	4-I	248-50	$C_{10}H_8IN_3O_2S$	11.7	11.6
14.	2,4-(CH₃)₂	180-82	$C_{12}H_{13}N_3O_2S$	16.7	16.8
15.	2-CH₃-4-Cl	163-65	$C_{11}H_{10}ClN_3O_2S$	15.1	14.8
16.	2-CH₃-5-Cl	165-67	$C_{11}H_{10}ClN_3O_2S$	14.1	14.8

* All the melting points are uncorrected.

TABLE 3—S-(4-ARYL-4H-1,2,4-TRIAZOL-3YL) 2-MERCAPTOMETHYL BENZIMIDAZOLE

S. No.	R	M.P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	H	232-35	$C_{16}H_{13}N_5S$	22.7	22.8
2.	2-CH₃	169-71	$C_{17}H_{15}N_5S$	22.0	21.8
3.	3-CH₃	174-77	$C_{17}H_{15}N_5S$	21.9	21.8
4.	4-CH₃	188-94	$C_{17}H_{15}N_5S$	22.4	21.8
5.	2-OCH₃	228-30	$C_{17}H_{15}N_5OS$	21.5	20.7
6.	3-OCH₃	176-80	$C_{17}H_{15}N_5OS$	20.7	20.7
7.	4-OCH₃	227-29	$C_{17}H_{15}N_5OS$	21.1	20.7
8.	2-Cl	211-13	$C_{16}H_{12}ClN_5S$	20.4	20.5
9.	3-Cl	173-74	$C_{16}H_{12}ClN_5S$	21.1	20.5
10.	4-Cl	212-14	$C_{16}H_{12}ClN_5S$	20.4	20.5
11.	3-CF₃	184-85	$C_{17}H_{12}F_3N_5S$	18.7	18.9
12.	4-Br	223-25	$C_{16}H_{12}BrN_5S$	17.4	18.1
13.	4-I	225-27	$C_{16}H_{12}IN_5S$	16.1	16.2
14.	2,4-(CH₃)₂	179-81	$C_{18}H_{17}N_5S$	20.4	20.8
15.	2-CH₃-4-Cl	133-36	$C_{17}H_{14}ClN_5S$	20.0	19.7
16.	2-CH₃-5-Cl	160-62	$C_{17}H_{14}ClN_5S$	19.2	19.7

* All the melting points are uncorrected

TABLE 4—S-(4-ARYL-4H-1,2,4-TRIAZOL-3YL) 2-MERCAPTOMETHYL-5-CHLOROBENZIMIDAZOLE

S. No.	R	M.P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	H	203-05	$C_{16}H_{12}ClN_5S$	20.7	20.5
2.	2-CH₃	159-61	$C_{17}H_{14}ClN_5S$	19.5	19.7
3.	3-CH₃	201-06	$C_{17}H_{14}ClN_5S$	20.1	19.7
4.	4-CH₃	209-11	$C_{17}H_{14}ClN_5S$	20.0	19.7
5.	2-OCH₃	164-68	$C_{17}H_{14}ClN_5OS$	19.6	18.8
6.	3-OCH₃	182-87	$C_{17}H_{14}ClN_5OS$	18.8	18.8
7.	4-OCH₃	210-12	$C_{17}H_{14}ClN_5OS$	19.0	18.8
8.	2-Cl	187-89	$C_{16}H_{11}Cl_2N_5S$	18.7	18.6
9.	3-Cl	218-20	$C_{16}H_{11}Cl_2N_5S$	19.1	18.6
10.	4-Cl	209-10	$C_{16}H_{11}Cl_2N_5S$	19.1	18.6
11.	3-CF₃	145-47	$C_{17}H_{11}F_3ClN_5S$	17.4	17.3
12.	4-Br	213-15	$C_{16}H_{11}BrClN_5S$	16.2	16.6
13.	4-I	227-28	$C_{16}H_{11}ClIN_5S$	15.7	15.0
14.	2,4-(CH₃)₂	212-14	$C_{18}H_{16}ClN_5S$	19.0	18.9
15.	2-CH₃-4-Cl	203-05	$C_{17}H_{13}Cl_2N_5S$	17.6	18.0
16.	2-CH₃-5-Cl	165-67	$C_{17}H_{13}Cl_2N_5S$	18.4	18.0

* All the melting points are uncorrected.

Acknowledgement

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Cycloaddition of the Thiol Group to Schiff Base Systems

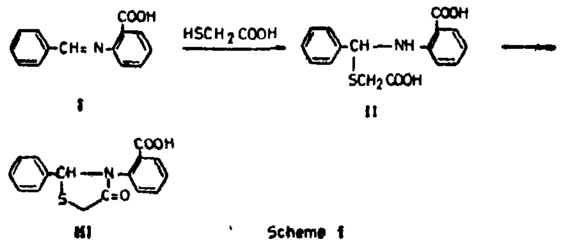
A. K. EL-SHAFEI*, KH. M. HASSAN and H. S. EL-KASHEF

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Manuscript received 5 August 1976, revised 20 December 1976, accepted 18 March 1977

Cycloaddition of arylidene-2-(aminothiazole IV, aminopyridine V) and arylidene-10-(hydrazinoacetyl) phenothiazine VI, with mercaptoacetic acid was attempted. It has been found that substituted 4-thiazolidones (X, XI and XII) can be obtained from the reaction of Schiff bases (IV, V and VI) with mercaptoacetic acid in dry benzene.

ALTHOUGH the addition of the thiol group to Schiff bases where subsequent cyclization is possible, as in the case of thiazolidone formation, has been well established in several investigations[1-4]; comparatively few instances have been reported wherein a simple addition product (scheme 1, structure II) has been obtained[2].



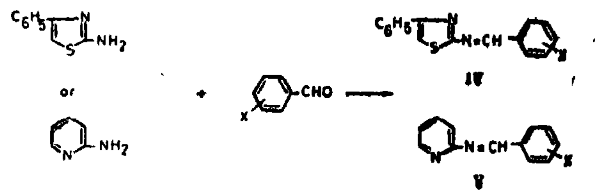
Scheme 1

Surrey[1] observed that the expected thiazolidone III, which was the usual type of product in other Schiff bases investigated was not obtained by the interaction of mercaptoacetic acid and benzalanthranilic acid. Rather, a substance resulted having the composition of the supposed intermediate II, which corresponded to a simple addition product of the thiol and Schiff base. The structure II for this addition product, although, not rigorously confirmed, seems quite reasonable, particularly in the light of other reactions involving Schiff bases[5-7].

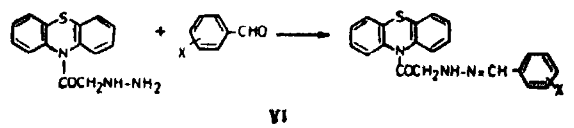
Several substituted 4-thiazolidones have been investigated by Surrey[3] and Troutman and Long[4], and are particularly interesting as local anesthetic and anticonvulsant agents. Owing to the latter potential medicinal importance of this class of compounds, this has led us to extend the interest in finding new and efficient routes to the synthesis of functionally substituted 4-thiazolidones.

We have recently shown[8] that reactions of nitro-substituted arylidene-2-aminothiazoles with diazomethane afforded 1,2,3-triazolines. We now report the extension of these studies on the unsaturated center in the hereby used Schiff bases (IV, V and VI) in the formation of new substituted 4-thiazolidones (X, XI and XII).

Arylidene-2-aminothiazoles and 2-aminopyridines were prepared by the interaction of 4-phenyl-2-aminothiazole or 2-aminopyridene with substituted aromatic aldehydes. The reaction proceeded smoothly in ethanol and in the presence of piperidine as a catalyst giving a quantitative yield of the corresponding Schiff bases (IV and V, cf. Table 1).

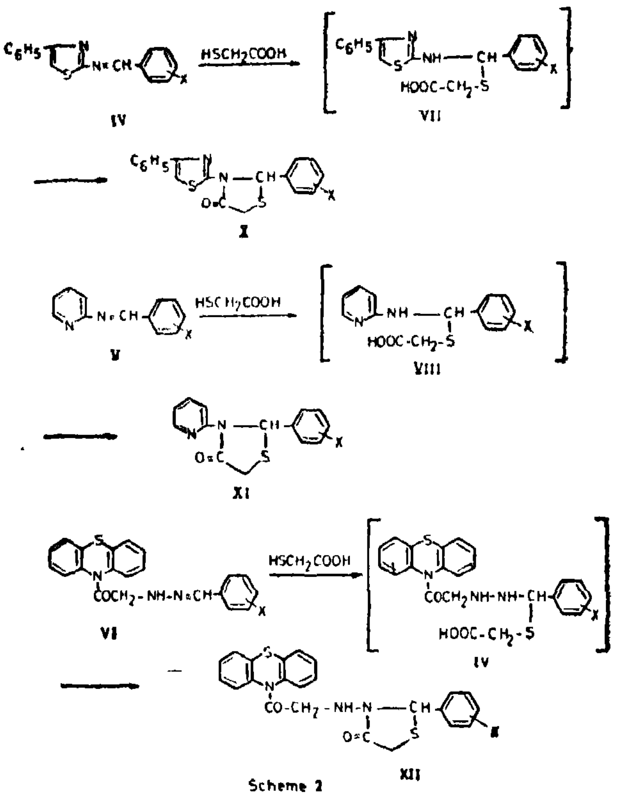


Arylidene-10-(hydrazinoacetyl) phenothiazine (VI) were prepared by the condensation of 10 (hydrazinoacetyl) phenothiazine with aromatic aldehydes in glacial acetic acid.



The action of mercaptoacetic acid on Schiff bases (IV, V and VI) was studied. The compounds obtained from this reaction were 4-thiazolidones (X, XI and XII) which are in agreement with the data given by Surrey[1,3]. The reaction proceeded smoothly in dry benzene by stirring the reaction mixture over periods of time varying from ½ an-hour to 3 hours.

* Chemistry Department, Faculty of Science, Sohag, EGYPT



Scheme 2

Substituted 4-thiazolidones (X, XI and XII) have been identified by a combination of elemental and spectral (IR) analysis. The infrared of 4-thiazolidones (X and XI) are characterized by a band in the region of 1700-1695 cm^{-1} which is attributed to the stretching vibration of C=O group; whereby 4-thiazolidones XII, show well definedabsorption band at 1695 cm^{-1} due to C=O group and -NH absorption band at 3450 cm^{-1}."

Experimental

All melting points were uncorrected and were obtained on a Kopfler electrically heated melting point apparatus. Infrared spectra were recorded on a Pye Unicam IR spectrophotometer, SP 200G, using KBr discs.

Arylidene-2-aminothiazoles (IV) and *arylidene-2-aminopyridines* (V): A mixture of equimolecular quantities of 4-phenyl-2-aminothiazole or 2-aminopyridine and aldehyde in 50 ml ethanol and 0.2 ml piperidine was refluxed for 2 hours. The reaction mixture was then concentrated and the product which separated on cooling was filtered off at the pump. The product was crystallized from the proper solvent. The results are listed in Table 1.

Arylidene-10-(hydrazinoacetyl) phenothiazines (VI) A mixture of equimolecular quantities of 10-hydrazinoacetyl)-phenothiazine and aldehyde in 50 ml glacial acetic acid was refluxed for 6 hours. The reaction mixture was poured, after cooling, in 300 ml of cold water where a solid mass was separated. The product was filtered off, washed with cold water and then crystallized from the proper solvent. The results are listed in Table 1.

4-Thiazolidones (X), (XI) and (XII): 0.06 mole of mercaptoacetic acid was added to a well stirred solution of 0.05 mole of Schiff base in 75 ml of dry benzene. The mixture was stirred over periods of time varying from ½ an hour to 3 hours. The product which precipitated was filtered off and crystallized from the proper solvent. The results are listed in Table 2.

TABLE 1—ARYLIDENE-2-(AMINOTHIAZOLE IV, AMINOPYRIDINE V) AND ARYLIDENE-10-(HYDRAZINOACETYL) PHENOTHIAZINE VI.

Compound No.	X	M.P. °C	Yield %	Mol. Formula	Analytical data Calculated % C	H	N	Observed % C	H	N
IVa	OCH_3	132-3	85	$C_{17}H_{14}N_2SO$	69.39	4.76	9.52	69.45	4.55	9.76
b	*o*-OH	120-2	90	$C_{16}H_{12}N_2SO$	68.57	4.29	10.00	68.33	4.05	10.25
c	$N(CH_3)_2$	95-8	90	$C_{18}H_{17}N_3S$	70.36	5.54	13.68	70.05	5.33	13.59
d	*m*-NO_2	113-4	75	$C_{16}H_{11}N_3O_2S$	62.14	3.56	13.59	62.32	3.69	13.70
e	*p*-NO_2	15'-5	76	$C_{16}H_{11}N_3O_2S$	62.14	3.56	13.59	62.05	3.73	13.45
Va	H	103-5	65	$C_{12}H_{10}N_2$	79.12	5.49	15.38	79.00	5.35	15.15
b	OCH_3	[illegible]5-8	68	$C_{13}H_{12}N_2O$	73.58	5.66	13.21	73.35	5.45	12.98
c	*o*-OH	66	92	$C_{12}H_{10}N_2O$	72.73	5.05	14.14	72.67	4.95	14.06
d	$N(CH_3)_2$	73	93	$C_{14}H_{15}N_3$	74.67	6.67	18.67	74.55	6.59	18.55
e	*o*-NO_2	124-5	65	$C_{12}H_9N_3O_2$	63.44	3.96	18.50	63.39	3.88	18.35
f	*m*-NO_2	105-7	68	$C_{12}H_9N_3O_2$	63.44	3.96	18.05	63.35	3.78	18.39
VIa	OCH_3	175	65	$C_{22}H_{19}N_3SO_2$	67.87	4.88	10.79	67.75	4.72	10.67
b	*o*-OH	170	68	$C_{21}H_{17}N_3SO_2$	67.20	4.53	11.20	66.88	4.45	11.05
c	*p*-OH	173-4	70	$C_{21}H_{17}N_3SO_2$	67.20	4.53	11.20	67.33	4.62	11.25
d	$N(CH_3)_2$	169	75	$C_{23}H_{22}N_4SO$	68.66	5.47	13.93	68.51	5.33	13.81
e	*p*-NO_2	147-8	63	$C_{21}H_{16}N_4SO_3$	62.38	3.96	13.86	62.25	3.85	13.71
f	C_6H_4-Fe-C_5H_5	195-6	60	$C_{25}H_{21}N_3SOFe$	64.24	4.50	8.99	64.05	4.35	8.76

TABLE 2—4-THIAZOLIDONES (X, XI AND XII) DERIVED FROM SCHIFF BASES IV, V AND VI RESPECTIVELY.

Compound No.	X	M.P. °C	Yield %	Mol. Formula	Analytical data Calculated % C	H	N	S	Observed % C	H	N	S
Xa	OCH_3	166-7	45	$C_{19}H_{16}N_2S_2O_2$	61.96	4.35	7.61	17.39	61.88	4.25	7.48	17.28
b	*o*-OH	209	50	$C_{18}H_{14}N_2S_2O_2$	61.02	3.95	7.91	18.08	60.85	3.75	7.79	17.94
c	$N(CH_3)_2$	188	50	$C_{20}H_{19}N_3S_2O$	62.99	4.99	11.02	16.80	62.78	4.85	10.87	16.70
d	*m*-NO_2	175-6	35	$C_{18}H_{13}N_3S_2O_3$	56.40	3.39	10.97	16.71	56.31	3.28	10.88	16.66
e	*p*-NO_2	163-4	35	$C_{18}H_{13}N_3S_2O_3$	56.40	3.39	10.97	16.71	56.35	3.45	11.06	16.69
XIa	H	98-9	35	$C_{14}H_{12}N_2SO$	65.63	4.69	10.94	12.50	65.45	4.51	10.82	12.35
b	OCH_3	117-8	35	$C_{15}H_{14}N_2SO_2$	62.94	4.90	9.79	11.19	62.82	4.75	9.65	11.00
c	*o*-OH	45	55	$C_{14}H_{12}N_2SO_2$	61.76	4.41	10.29	11.76	61.62	4.62	10.32	11.82
d	$N(CH_3)_2$	61-3	60	$C_{16}H_{17}N_3SO$	64.21	5.69	14.05	10.70	64.12	5.72	13.95	10.61
e	*o*-NO_2	140	43	$C_{14}H_{11}N_3SO_3$	55.81	3.65	13.95	10.63	55.73	3.57	13.82	10.52
f	*m*-NO_2	153	45	$C_{14}H_{11}N_3SO_3$	55.81	3.65	13.95	10.63	55.92	3.59	13.88	10.72
XIIa	OCH_3	183-4	25	$C_{24}H_{21}N_3S_2O_3$	62.20	5.54	9.07	13.82	62.02	5.72	8.89	13.75
b	*o*-OH	182-3	22	$C_{23}H_{19}N_3S_2O_3$	61.47	4.23	9.35	14.25	61.22	4.12	9.15	14.09
c	*p*-OH	184-5	25	$C_{23}H_{19}N_3S_2O_3$	61.47	4.23	9.35	14.25	61.35	4.32	9.25	14,28
d	$N(CH_3)_2$	180-1	32	$C_{25}H_{24}N_4S_2O_2$	63.03	5.04	11.76	13.45	62.85	5.15	11.69	13.39
e	*p*-NO_2	137-8	20	$C_{23}H_{18}N_4S_2O_4$	57.74	3.77	11.72	13.39	57.69	3.68	11.69	13.46
f	C_5H_4-Fe-C_5H_5	185-6	20	$C_{27}H_{25}N_3S_2O_2Fe$	59.89	4.25	7.76	11.83	60.11	4.32	7.68	11.89

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Notes

Proton-Ligand Formation Constants and Formation Constants of Some Tl(I)-Amino Salicylates.

P. V. KHADIKAR

School of Studies in Chemistry, Vikram University, Ujjain (M.P.)

and

P. S. DESMUKH*

Govt. College, Khargone, (M.P.).

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COMPLEXING tendencies of Tl(I) with 4-amino salicylic (4-ASA) and 5-amino salicylic (5-ASA) acid have been studied in the present work. Proton ligand formation constants required for the calculation of formation constants were determined under the same experimental conditions employing half integral (HI), linear plot (LP), and point-wise calculation (PC) methods. Refined values of formation constants were also calculated by the method of least-squares (LS).

Experimental

*p*H-metric titrations of solutions of (i) free $HClO_4$, (ii) free $HClO_4$ + ligand and (iii) free $HClO_4$ + ligand + Tl(I), were performed in 50% (V/V) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at $0.1M$ ($NaClO_4$).

The experimental set up and the method of calculation is the same as described earlier[7-9].

Results and Discussion

The Irving-Rossotti expression[10] was used for the calculation of $\bar{n}_A$, $\bar{n}$ and p(L). In calculatin of $\bar{n}_A$, $\bar{n}$ and p(L), the concentrations were corrected for the changes in volume as a result of addition of alkali during titrations. A series of values of $\bar{n}_A$, $\bar{n}$ and p(L) corresponding to different B-values (*p*H-meter readings) were calculated and formation curves were obtained for ligands and complexes by plotting $\bar{n}_A$ vs. *p*H and $\bar{n}$ vs. p(L) respectively.

The values of log K_1^H, log K_2^H and log K_3^H were directly read from the proton ligand formation curves by half integral method. Linear plot and pointwise calculation methods were also used for calculating proton ligand formation constants (Table-1). Results cleary indicate the protonated nature of amino group. Values are in agreement with the resonance, inductive and steric effect of the groups in the two cases and are comparable to the values of other substituted salicylic acids under the same experimental conditions[8] and also to the values of other workers. In the present cases, values of log K_1^H, log K_2^H and log K^H_3 correspond to protonation of phenoxide, amino, and carboxylate group respectively.

In both the cases, $\bar{n}$ value never exceeds 1.75, indicating thereby the formation of only 1:1 and 1:2 complexes. The values of log K_1 and log K_2 were directly read from the formation curves as p(L) at $\bar{n}$ = 0.5 and 1.5 corresponding to log K_1 and log K_2 respectively. Formation constants were also calculated by employing linear plot and pointwise calculation method. Refined values of formation constants were obtained by the method of least squares (Table-2). The order of formation constant is in agreement with the basicities of the ligands. The values are higher than that of nitro derivatives[1,2,4-6] which may be due to less steric hindrance of amino group in comparison to nitro group[11] for Tl(I) ion.

In view of very low concentration of Tl(I) ion ($1\times10^{-4}M$) used in the titration, formation of polynuclear complexes may be ignored.

TABLE 1—PROTON LIGAND FORMATION CONSTANTS OF LIGANDS

METHOD	4-ASA			5-ASA		
	log K_1^H	log K_2^H	log K_3^H	log K_1^H	log K_2^H	log K_3^H
HI	10.92	5.96	2.80	11.00	5.45	2.80
LP	10.94	5.95	2.80	10.99	5.43	2.80
PC	11.20	5.94	2.78	11.66	5.45	2.72
AVERAGE	11.02	5.95	2.79	11.22	5.44	2.77

TABLE 2—FORMATION CONSTANTS OF Tl(I)-COMPLEXES

METHOD	Tl(I)-4-ASA		Tl(I)-5-ASA	
	log K_1	log K_2	log K_1	log K_2
HI	7.40	5.50	7.88	5.32
LP	7.30	5.55	7.86	5.34
PC	7.36	5.51	7.91	5.42
LS	7.32	5.54	7.88	5.36
AVERAGE	7.36	5.52	7.88	5.36

* For correspondence

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Calorie and Amino Acid Composition of *Cucurbita pepo* and *Cucumis melo* Seeds

S. S. JOSHI and R. K. SHRIVASTAVA

Department of Chemistry, Govt. College of Engg. and Tech., Raipur (M. P.)

and

S. S. NIGAM

Department of Chemistry, Saugar University, Sagar (M. P.)

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CUCURBITA pepo and *Cucumis melo* seeds are found to be rich in calorie, proteins and all protein bound essential amino acids except tryptophane.

Cucurbita pepo and *Cucumis melo* belong to the family "Cucurbitaceae". As described by Kirtikar and Basu[1], their fruit and mature seeds possess several medicinal properties. These seeds are used as nervine tonic. Because of little published information on the subject, high calorie and protein contents of these seeds, the nutritional characterstics of their protein isolates are investigated and reported in this communication.

Experimental

Proximate chemical composition was determined by standard methods[2-3]. The results are given in table 1.

TABLE 1—PROXIMATE CHEMICAL COMPOSITION OF *Cucurbita pepo* AND *Cucumis melo* SEEDS

SEEDS	Per 100 g. of edible portion						
	Mois-ture	Fats	Proteins	Fibre	Ash	Carbohydr-ates	Calorie
Cucurbita pepo	8.4	49.2	26.2	0.5	4.2	11.6	655
Cucumis melo	7.2	48.7	30.6	0.5	5.3	7.6	640

The coarsely ground seeds were defatted with petroleum ether (B.P. 60-80°) and the seed meals were analysed for N-contents. The seed meals of *Cucurbita pepo* and *Cucumis melo* were found to contain 66.8 and 68.2 percent of proteins. The defatted seeds were repeatedly extracted with cold alkaline 10°/₀ brine for several hours and filtered. The filtrate, on adjustment of *p*H-value between 3.5-4.5, precipitated proteins in yields 21.8 and 21.6°/₀ respectively from *Cucurbita pepo* and *Cucumis melo* seeds respectively. Proteins were hydrolysed completely by refluxing with a mixture of 6*N*.HCl and 80°/₀ formic acid taken in 1 : 1 ratio by volume and the hydrolysate concentrated to syrupy consistency by evaporation which was vacuum desiccated[4]. The mass was then dissolved in 10°/₀ isopropanol and qualitatively analysed by uni and two dimensional circular and vertical paper (Whatman No 1) and cellulose thin layer chromatographic techniques[6-11] using (1) n-butanol : acetic acid : water (4:1:1.6); (2) pyridine : water (4:1); (3) n-butanol : pyridine :

TABLE 2—AMINO ACID COMPOSITION OF PROTEIN ISOLATES OF *Cucurbita pepo* AND *Cucumis melo* SEEDS

(Amino acid percentage expressed in g/16 g of nitrogen)

% of Amino acid	*Cucurbita pepo*	*Cucumis melo*
Indispensable		
1. Lysine	6.14	4.63
1. Histidine	1.56	1.44
3. Threonine	7.2	6.4
4. Phenylalanine	6.02	7.40
5. Valine	9.0	9.8
6. Methionine	2.8	0.8
7. Tryptophane	0.3	0.4
8. Leucine and isoleucine	12.9	13.4
Semi-Indispensable		
9. Serine*	5.2	4.3
10. Glycine (indispensable for chicks)	8.4	8.1
11. Tyrosine †	4.2	1.42
12. Cystine ‡	0.4	0.6
13. Arginine (indispensable both for rats and chicks)	14	14.1
Dispensable		
14. Glutamic acid	10.2	11.8
15. Aspartic acid	6.2	8.2
16. Alanine	6.1	8.4
17. Proline §	0.8	0 5
18. γ-Amino butyric acid	Traces	Traces

Mean values of 10 determinations

* Serine exerts sparing effect upon glycine.
† Tyrosine exerts sparing effect upon phenylalanine.
‡ Cystine exerts sparing effect upon methionine.
§ Optical density measured at 440 nm.

water (1:1:1) and (4) phenol : water (3:1) as solvents and various specific spraying reagents[12-15]. Butanol-acetic acid-water in combination with pyridine-water/butanol-pyridine-water/phenol-water were used as solvents for developing two dimensional chromatograms. For quantitative determinations, ninhydrin colours of individual amino acids of the two dimensionally developed chromatogram were estimated photometrically[16] at 570 nm using a Bausch and Lomb Spectronic-20-Colorimeter. The results are given in Table 2.

A perusal of tables 1 & 2 revealed that the seeds of *Cucurbita pepo* and *Cucumis melo* are rich both in calorie and protein contents. Their proteins are rich in all essential amino acids particularly lysine, (phenylalanine + tyrosine), threonine, valine, (leucine and isoleucine) and (methionine + cystine) except tryptophane.

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Electroinitiated Post-polymerization of Methylmethacrylate using Sugar plus Acid as Supporting Electrolyte

ARUN K. SARKAR and SANTI R. PALIT

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India.

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If electric current is passed through a solution of sodium acetate containing methylmethacrylate(MMA) until the solution turns faintly hazy, a good yield of polymer can be obtained even after switching off the current at this stage, provided the system is allowed to stand undisturbed for a few hours[1]. This is termed Post-polymerization. Not many electrolytes are known to be efficient post-polymerization initiators and just a handful have been lately discovered[2].

We present here a preliminary report of a few binary initiators of anodic post-polymerization of methyl methacrylate, the individual components having no such power. Some inorganic acids, however, do have some power of cathodic post-polymerization under certain conditions[3], and dextrose has been used as a component of a redox initiator[4,5].

Results and Discussion

The experimental arrangement is more or less the same as described by Palit[1]. The electrolyte used is a solution of HCl containing a sugar. The solution is electrolysed to produce a faint haziness ; the current is then switched off and the system is left undisturbed for a day or so after which the post-polymer is collected. The initial haziness has to be just optimum ; if it is too strong there is a tendency towards gelation during post-polymerization, more so for cane sugar than for glucose.

Effect of concentration of dextrose and HCl is shown in Table 1 from which it is concluded that a

TABLE 1—EFFECT OF ACID AND DEXTROSE CONCENTRATION IN THE ELECTROINITIATED POST-POLYMERIZATION OF METHYLMETHACRYLATE USING DEXTROSE/HCl AS ELECTROINITIATOR ELECTROLYTE

[MMA]=1% (v/v), current=1000 mA × 60 mins., Temperature=32.5°C, Post-polymerization time=24 hrs.

Conc. of dextrose in (*M*) HCl=0.72 M	Post polymer yield(%)	[η] at 30°C
0.1	0.75	—
0.2	50.7	—
0.3	58.6	1.12
0.4	55.0	—
0.5	52.6	1.15
0.6	51.5	—
Conc. of HCl in (*M*) Dextrose=0.3 *M*		
0.60	36.8	0.95
0.72	58 6	1.12
0.84	63.5	1.28
1.20	73.7	insoluble gel

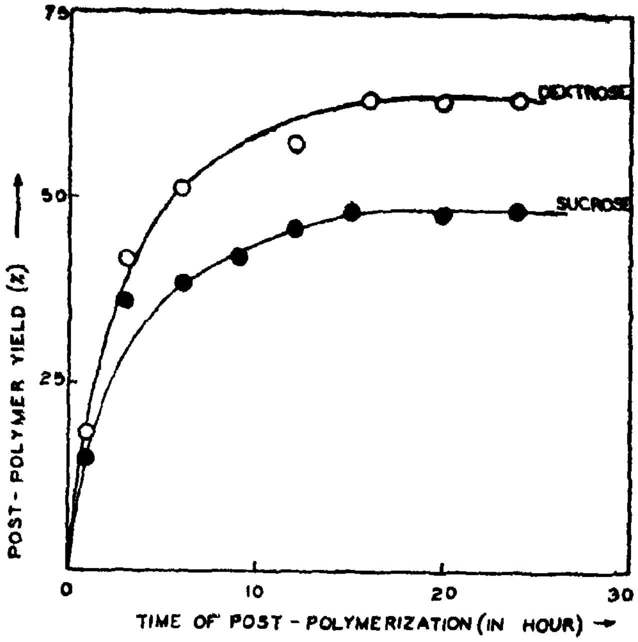


Fig. 1. Time versus per cent yield during Post-polymerization of Methylmethacrylate by Sugar/HCl as supporting electrolyte.
[HCl]=0.72*M*, [Sugar]=0.3*M* [MMA]=1%(v/v) Current=100 mA × 60 mins. temp.=32.5°.

sugar concentration of about 0. to 0.3 is just about the optimum and the minimum acid concentration necessary to produce a high yield is about 0.72 *M*. The post-polymerization is rather fast during the first few hours as is shown for a typical system in Fig. 1. The [η]-value however does not change much with progress of post-polymerization—a characteristic which is typical of post-polymerization.

Though aqueous redox polymerization is strongly inhibited by traces of dissolved oxygen, post-polymerization is not so sensitive to air, no special precaution being therefore necessary to exclude air in the latter case. So the reported post-polymerization does not involve redox polymerization. However, this is a free radical process as is shown by strong inhibition by hydroquinone. HCl has possibly a dual function, serving as the electrolyte as well as producer of the right *p*H. The sugar gets oxidised at the anode possibly producing the initiating free radical. It is likely that each monomer-swollen oligomeric free radical formed by electro initiation constitutes the isolated loci where post-polymerization takes place. The gelation appears to be due to the presence of sugar. It is likely that some kind of crosslinked polymer is formed due to multiple free radical formation (by oxidation or chain transfer) on the same sugar molecule.

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A Peculiar Current-Increasing Effect of Cellophane Membranes.

SANTI R. PALIT and SACHI DULAL SINHA

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur Calcutta-700032.

Manuscript received 24 September 1976, accepted 17 March 1977

IN course of our work on non-Faradaic electrolysis[1,2] we made the surprising observation that on interposing a cellophane membrane between the two electrodes, with the purpose of checking inter-electrode diffusion and convective or mechanical mixing, the current showed an increase (+ ΔI) instead of the expected decrease.

This can be easily observed with an experimental set-up as shown in Fig. 1 using water as the electrolyte.

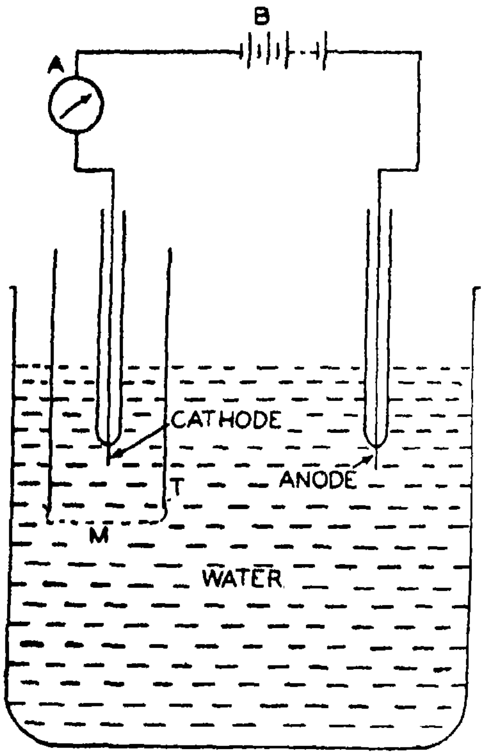


Fig. 1. Experimental set-up for studying the Current Increasing (+ Δi) effect of Cellophane Membrane (T = Glass or Plastic tube ; M = Cellophane Membrane ;

A = Ammeter (milli or micro as necessary);
B = Bank of Lead Accumulators or D. C. Power Supply).

When a constant D. C. voltage is applied between the two electrodes (without the interposed cellophane membrane as shown by the dotted line) the current slowly increases with time and tends to attain a more or or less steady value (Fig. 2, Curve 1). If the same experiment is repeated under exactly the same condition except that the cathode (i.e. mouth of tube T) is covered by a cellophane membrane shown by the dotted line, a large increase of current is observed instead of an expected decrease ; there is a large instantaneous increase and an enormous (nearly five times) eventual increase of current (*Fig. 2, Curve 2*). Using a plastic tube instead of the glass tube or using a cellophane sac to enclose the cathode gives the same kind of result. Instead of a cellophane membrane a good filter paper (Whatman No. 4) shows similar albeit much less + Δi effect. If the anode is enclosed instead of the cathode, the + Δi effect is very much less (compare curve 3 and 4). This + Δi-effect tends to vanish with increasing concentration of dissolved electrolyte.

At first we thought this to be due to the leaching out of some ionic impurity present in cellophane. However, *this did not seem possible for* various reasons.

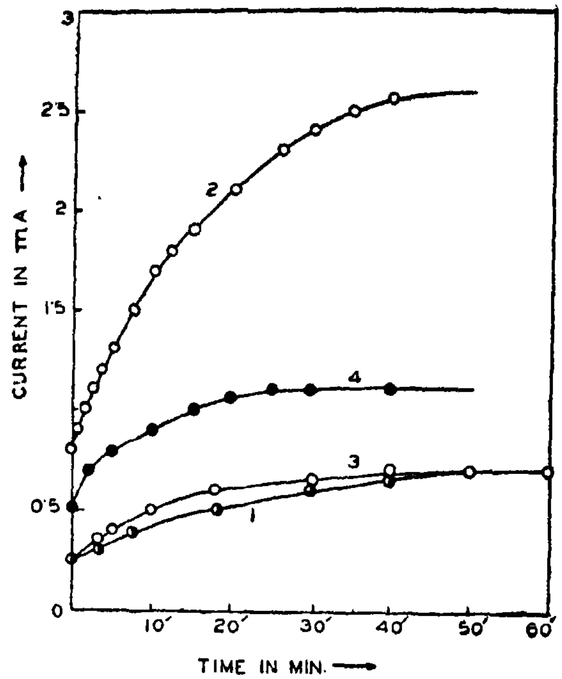


Fig. 2. Typical curves showing change of current on interposing cellophane membrane (Time variation also shown) (V = 200 Volts).

1. Cathode inside T but without cellophane.
2. Same as 1 but with cellophane membrane (M).
3. Anode inside T but without cellophane.
4. Same as 3 but with cellophane membrane (M).

Firstly, the cellophane used was pre-treated for days with repeated charges of hot conductivity water and the leach water did not show any ionic leaching by conductivity measurements. Secondly, by a suitable device the membrane could be removed from its position and again put in its place repeatedly and everytime a 'kick' in the microammeter needle could be observed. As a matter of fact if the tube T is dispensed with and a cellophane membrane is immersed near the cathode more or less covering the latter, a 'kick', though very small, of the microammeter needle is observed. It *appears that* cellophane by mere contact with water somehow increases its conductivity.

Since the 'leaching-out' *idea falls through*, we thought about the possibility of some electrolyte being formed near the enclosed electrode (viz. the cathode). This idea however fails to explain at least the initial almost instantaneous increase and also the *transient* nature of the increase ; besides the final increase appears to be too much *for such* an explanation. Also, it is difficult to see why the + Δi-effect is much stronger with cathode than with anode enclosed. But a crucial blow to such a theory is given by the fact that even very low A.C also shows this + Δi-effect (see later).

It appears that for an explanation we have to look for a different mechanism of current conduction than the conventional one. Since this + Δi-effect is stronger

with dilute solution and low current, and since we have demonstrated that many anomalous features accompany electrolysis under this condition (called non-Faradaic electrolysis[1-3]), it is likely that the explanation in these two cases may have something in common. Since hydrated electron formation near the cathode has been one of the suggested explanations of non-Faradaic electrolysis we may assume that a steady state concentration of hydrated electrons builds up inside the cathode chamber, which leak out leading to the enhancement of current. This is theoretically possible because electrons are being pumped in at the rate of about 10^{15} electrons/sec at about 1 mA whereas the hydrated electrons get annihilated at a rate constant of the order of 10^{9}-10^{11} per sec. So the cathode chamber after some time becomes a veritable storehouse of electrons which leak out at a much faster rate than the migration speed of ions. So electronic conduction takes place along with ionic conduction and is responsible for the $+\triangle i$-effect. This build-up of electrons near the cathode which is almost instantaneous is responsible for the observed reduction of dissolved nitrogen to ammonia in a similar apparatus as reported by Palit[4].

Any way, it appears that some kind of extra 'pumping' action of charged carriers under the action of an electric field comes into play on interposition of a cellophane membrane particularly near the cathode.

Since a good portion of the $+\triangle i$ is instantaneous it is expected that A.C. would also show this $+\triangle i$-effect. We have found this to be true with two kinds of experiments. Firstly, by using mains A.C. we have found that by simple immersion of a cellophane membrane between two electrodes, with water as the electrolyte, there is an upward 'kick' of the microammeter and on subsequent removal of the cellophane a downward 'kick'; and this could be repeated any number of times. Secondly, the measured conductivity of water with a conventional A.C. bridge increases by nearly a factor of two when a cellophane membrane is dipped inside the conductivity cell between the two electrodes; furthermore this change is found to be reversible. It is evident that the current conduction mechanism through water or a poorly conducting solution changes considerably in the presence of a cellophane membrane in a way which is rather difficult to understand.

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Some Observations on the Electronic Spectra of Terpyridyl Copper Chloride.

K. BANERJEE and S. K. BOSE

Department of Pure Chemistry, University College of Science, Calcutta-9, India

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THE commonest structure of the pentacoordinated complexes of metals is a trigonal bipyramid (D_{3h}) although a few square pyramidal structures are known. The most well-known example of a trigonal bipyramidal complex of copper is monoterpyridyl copper chloride. Although the earlier[1] x-ray data suggested that zinc terpyridyl complex is a distorted trigonal bipyramid, with which the copper complex is isomorphous, the latter work[2] indicates the structure to be square pyramid. Each unit cell contains two complex molecules, the chlorine atom of the second molecule coordinates (called hydrogen bonded) with the copper atom of the first giving an effectively bridged structure. In the latter case we have effectively hexacoordinated complexes with three N and three Cl atoms surrounding the copper atom commonest symmetry of such a structure will be D_3. X-ray study by Goldschmid and Stephenson[3] shows Zn (terpy) Cl_2 to have 62% trigonal bipyramidal character. Einstein and Penfold[4] have shown Zn (terpy) Cl_2 has five coordinated trigonal bipyramidal structure.

An ideal trigonal bipyramidal structure has the symmetry D_{3h} and from the d orbital energy level scheme[5] for a d^9 atom such as copper (a system with one hole) two transitions are expected, viz. $^2E' \leftarrow {}^2A_1'$ and $^2E'' \leftarrow {}^2A_1'$, the latter is electronically forbidden. If instead we regard the complex to be trigonal (D_3), then we expect the following transitions $^2A_1 \leftarrow {}^2E$ (xy polarised) and $^2E \leftarrow {}^2E$. The latter will split into two transitions of species A and E one being Z and the other xy polarised.

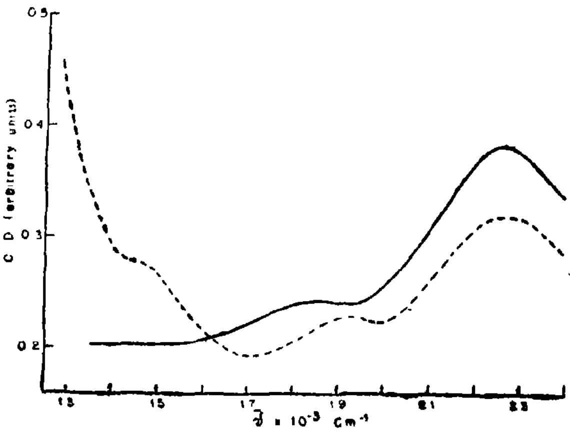


Fig. 1. Absorption spectra of powdered crystals of [Zn (Terpy)] Cl_2 (———) and powdered crystals of [Zn (terpy)] Cl_2, [Cu(terpy)] Cl_2 (- - - - - -)

Good single crystal of Cu (terpy) Cl_2 itself could not be grown. So the absorption spectra of polycrystalline Cu (terpy) Cl_2 in the host lattice of Zn (terpy) Cl_2 were recorded in a set up described by Chakraborty and Basu[6]. Spectra of powdered Zn (terpy) Cl_2 (Fig. 1) show band at 22650 cm^{-1} and 18000 cm^{-1}. Single crystal of Cu (terpy) Cl_2 in the host lattice of Zn (terpy) Cl_2 were then powdered and its recorded spectra show a new band at 14800 cm^{-1}. This new band is due to the copper complex and is in close agreement with the solution spectral data[7] which shows one absorption band at 680 mμ (14440 cm^{-1}) with $E_M = 80$.

The crystal spectra of a single crystal of the copper complex in the host lattice of the zinc complex with light polarised along the long and short axis of the crystal (Fig. 2), show two bands at 14500 cm^{-1} and 14110 cm^{-1} appearing in both states of polarization while a weak band at 16600 cm^{-1} occurs only in one state of polarization.

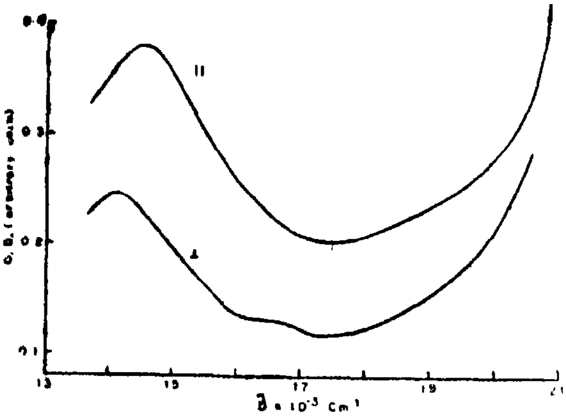


Fig. 2 Absorption spectra of a single crystal of [Zn(terpy)] Cl_2. [Cu(terpy)]Cl_2 in polarised light.

The spectral data, therefore, are in conformity with a distorted trigonal bipyramidal structure for Cu (terpy) Cl_2.

Acknowledgement

We thank Prof. S. Basu for discussions during the course of the work.

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Determination of Carboxylic Acids Via Formation of Benzylthiuronates.

J. V. KRISHNA REDDY and K. S. BOPARAI

School of Studies in Chemistry, Vikram University, Ujjain, 456 010

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CHARACTERIZATION of carboxylic acids as benzylthiuronates[1] is valuable, however, the melting points of many of these salts lie within a narrow range of temperature and the values also depend on the experimental technique employed for the determination. Therefore, it is often desirable that the identification may be confirmed by some independent method. Titrimetric determination of benzylthiuronates with perchloric acid[2] in anhydrous acetic acid medium using crystal violet indicator affords a useful method for the determination of equivalent weights of the corresponding acids. The water of crystallization present in certain salts can interfere with the determinations. Further, the method suffers from the usual shortcomings of non-aqueous titrimetry. Benzylisothiourea, which is liberated when benzylthiuronates are treated with alkali, undergoes spontaneous decomposition to benzylmercaptan which can be estimated titrimetrically with sodium *o*-hydroxymercuri benzoate[3] using thiofluorescein indicator ; the procedure, however, has been tested with a few carboxylic acids only. The decomposition of benzylisothiourea to benzyl mercaptan has been found to be quantitative and the iodimetric determination of the latter is an accurate procedure for the determination of equivalent weights of carboxylic acids. The method was tested on benzylthiuronium chloride and benzylthiuronates of carboxylic and sulphonic acids. Unlike the Berger's procedure, the present method is applicable to sulphonic acids as well. The accuracy of the procedure is comparable to that of Berger's. Further, the procedure is convenient as it is devoid of the shortcomings of the non-aqueous procedure. The procedure is particularly valuable in the case of an acid which is not available in the pure form and direct titrimetric determination with a base is not sufficiently accurate. As such, the procedure merits recommendation. The results are recorded in Table 1.

Experimental

Determination of Benzylthiuronates.

Benzylthiuronates are prepared according to the reported procedure[1]. The salt (75 to 200 mg) is weighed into an iodine flask and dissolved in 20% ethanol. Sodium hydroxide (10 ml, 10% W/V) is introduced and the contents of the flask are swirled for a few minutes. Hydrochloric acid (10 ml, 3N) is then added to acidify the solution. A little more ethanol is added if the solution becomes cloudy. The solution is titrated against 0.05 N iodine using starch indicator.

TABLE 1—DETERMINATION OF BENZYLTHIURONATES

Benzylthiuronium	Equivalent Weight Calculated	Found*	Deviation (%)**	
Chloride	202.63	202.94	+0.15	
Oxalate	211.17	211.75	+0.27	0.6
Propionate	240.21	239.65	−0.23	0.2
n-Butyrate	254.23	253.13	−0.44	0.4
Monochloroacetate	260.65	261.45	+0.31	0.4
n-Valerate	268.24	268.00	−0.09	0.1
Benzoate	288.21	289.10	+0.31	
p-Aminobenzoate	303.23	302.14	−0.36	
Salicylate	304.21	305.54	+0.44	
Cinnamate	314.23	312.75	−0.47	
Benzene sulphonate	324.27	322.95	−0.33	
p-Toluene sulphonate	338.29	339.42	+0.31	
Sulphanilate	339.29	340.35	+0.41	
p-Chloro benzene sulphonate	358.72	359.58	+0.24	
Naphthalene-1-sulphonate	374.28	373.56	−0.19	

* Average of two or three determinations.
** Reported by Berger.

Acknowledgement

The authors are grateful to Prof. M. M. Bokadia for providing the necessary research facilities and to C.S.I.R. (India) for the award of a research fellowship (to J. V. K. R.).

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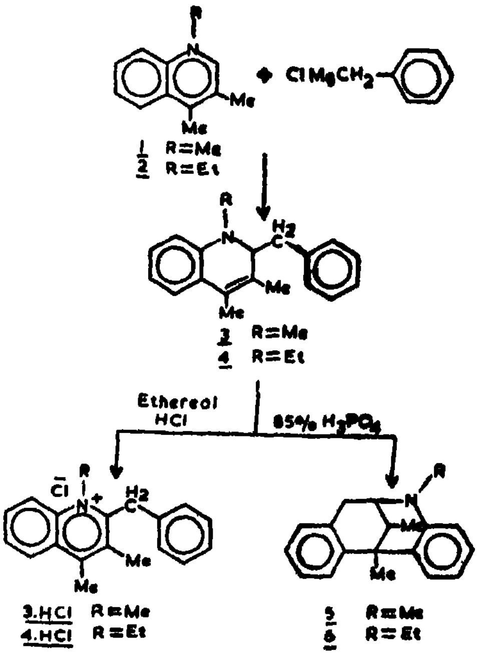
Studies on Morphine and Related Compounds : Synthesis of 2,5,9-Trimethyl and 2-Ethyl-5, 9-Dimethyl-3 4 : 6,7-Dibenzomorphans

RAJENDRA SHARMA, V. K. GOYAL, R. P. TYAGI
and
B. C. JOSHI*

Chemical Laboratories, University of Rajasthan, Jaipur, 302004.

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2,5,9-trimethyl-3, 4 : 6, 7-dibenzomorphan (5) and 2-ethyl-5,9-dimethyl-3,4 : 6,7-dibenzomorphan (6) were synthesised by condensing 1,3,4,-trimethyl quinolinium iodide (1) and 1-ethyl-3,4,-dimethyl quinolinium iodide (2) separately with benzyl magnesium chloride under Freund's reaction conditions[1] followed with subsequent cyclisation of corresponding 1,2-dihydro products (3) and (4) with 85°/。 H_3PO_4. The purity of these compounds was ascertained through tlc examination. The structures of 3 and 4 as hydrochlorides, 5 and 6 as bases were established through elemental and spectral studies.



Experimental

Melting points are uncorrected, spectral studies were done at chemical laboratories, University of Rajasthan, Jaipur. Nmr spectra were recorded on Perkin–Elmer R12B spectrometer using TMS as internal reference standard. (Chemical shifts expressed in δ ppm). Microanalyses were done at CDRI, Lucknow.

* Present Address : Professor & Head, Department of Chemistry, Garhawal University, SRINAGAR (U.P.)

2,5,9-Trimethyl-3,4 : 6,7-Dibenzomorphan (5)

To a suspension of 1,3,4-trimethyl quinolinium iodide (1) (5.98g., 0.03*M*) in absolutely dry ether, benzyl magnesium chloride (benzyl chloride 3.78g., 0.3*M* ; magnesium 0.72g, 0.03*M* ; ether 50 ml) was added within 15 min. with continuous stirring. The reaction mixture was further stirred continuously for 4 hr at 10-15° and another 4 hr at 30-40°. The reaction mixture was left overnight. This was treated in usual manner[4], and was distilled at 140-50°/0.3 mm., when an oily substance 3 was obtained [Yield 2 10g., (40%)]. As the dihydro compounds are generally unstable, a small portion of it was converted to 3.HCl for identification (m.p. 125°) and rest of the oily compound was subjected to cyclization with 85% H_3PO_4 at 140-60° for 48 hr. The reaction mixture on usual treatment[4] gave a crude product which was distilled under reduced pressure 160-65°/0.3 mm. to give a white solid base 5 and was crystallized with acetone-pet. ether mixture, yield, 0.672g., (32%), m.p. 135°. 5 was converted to its hydrochloride salt (m.p. 120°), foliage green picrate (m.p. 160-65°) and in small white needles of methiodide (m p. 242-45°). The purity of 5 was ascertained through tlc by using Silica Gel-G as adsorbent and acetone-pet-ether (1 : 9) as mobile phase

Rf = 0.62.

Analyses :

Found $C_{19}H_{21}N$ (5)

C, 86.58 ; H, 7.86 ; N, 5 58%.

Calcd. C, 86.69 ; H, 7.98 ; N, 5.33%.

2-Ethyl-5,9-Dimethyl-3,4 : 6,7-Dibenzomorphan (6)

On similar lines as followed in the synthesis of 5, 1-ethyl-3,4-dimethyl quinolinium iodide (2)(6.26g,0.02*M*) was reacted with benzyl magnesium chloride (benzyl chloride 3.795g., 0.03*M* ; Magnesium 0.72g., 0.03*M* ; ether 50 ml) and the dihydro compound 4 b.p. 150-155°/0.3 mm, Yield 1.98g (38%) was obtained. A small portion of 4 was converted to its hydrochloride salt 4 HCl (m.p. 120°) and the rest was cyclized with 85% H_3PO_4 at 140-60° for 48 hr. The crude base thus obtained was distilled at 162-65°/0.3 mm to give a white solid 6. It was crystallised from acetone-pet. ether mixture m.p. 140°, Yield 0.594 g (30%). 6 was converted to its hydrochloride salt (m.p. 110°), foliage green picrate (m.p. 175°) and methiodide (m.p. 270°). The purity of 6 was ascertained through tlc using the same solvent system as for 5 (Rf = 0.67).

Analysis :

Found : $C_{20}H_{23}N$ (6).

C, 86.82 ; H, 8.42 ; N, 4.88%.

Calcd. C, 86.64 ; H, 8.30 ; N, 5.06%.

Discussion

The present communication deals with the synthesis of 5 and 6, compounds related to 6,7-benzomorphan with an additional fusion of benzene ring at position 3 and 4. The synthesis of these compounds was an attempt to synthesise metazocine and etazocine analogs (compounds related to 6,7-benzomorphan)[2] to see the pharmacological activity of these compounds. 1,3,4-

TABLE 1—NMR SPECTRAL DATA (CHEMICAL SHIFTS EXPRESSED IN δ PPM)

Compound Number	Molecular formula	Aromatic protons.	$C-CH_3$	$N-CH_3$	$-CH$	$-CH_2$	$N-CH_2$
3-HCl	$C_{19}H_{20}NCl$	6-9-8.45 9H	2.72(s) 3H	4.25(s) 3H	–	4.6 2H	-
			2.4(s) 3H				
4-HCl	$C_{20}H_{22}NCl$	6.9-8.45 9H	2.72(s) 3H	0.97(t) 3H		4.1-4.6 4H	
			2.4(s) 3H			2H	2H
5	$C_{19}H_{21}N$	6.4-7.7 8H	1.1(d) 3H	2.1-3.8 7H			
			1.82(s) 3H 3H		1H(C_1) 1H(C_9)	2H	
6	$C_{20}H_{23}N$	6.4-7.7 8H	1.85(s) 3H				
			0.9-1.5 6H			2.9-3.8 6H	
			3H 3H		1H(C_1) 1H(C_9)	2H	2H

S=singlet, d=doublet ; t=triplet.

Trimethyl quinolinium iodide (1) and 1-ethyl-3, 4-dimethyl quinolinium iodide (2) were reacted with benzyl magnesium chloride separately under Freund's reaction conditions[1]. The unstable 1,2-dihydro products 3 and 4 (presumably formed) obtained after usual treatments[4] were distilled under reduced pressure. Small portions of these were converted to their hydrochloride salts, 3.HCl and 4.HCl, with ethereal-HCl. The rest were immediately kept for cyclisation with 85% H_3PO_4[3] separately. 3.HCl and 4.HCl were identified as 2-benzyl-1,3,4-trimethyl quinolinium chloride and 2-benzyl-1-ethyl-3, 4-dimethyl quinolinium chloride respectively. It has also been reported earlier that 2-benzyl-1,4-dimethyl-1-2-dihydroquinoline rearranged to-benzyl-1,4-dimethyl quinolinium chloride[4] and such rearrangements were also observed[5]. The purity of 3.HCl, 4.HCl, 5 and 6 were ascertained through tlc.

Nmr spectral data of 3.HCl, 4.HCl. 5 and 6 have been given in Table No. 1. The structures to these compounds were assigned as follows :-

3.HCl 2-Benzyl-1,3,4-trimethyl quinolinium chloride.

4.HCl 2-Benzyl-1-ethyl-3,4-dimethyl quinolinium chloride.

5 2,5,9-Trimethyl-3,4 : 6,7-dibenzomorphan.

6 2-Ethyl-5,9-dimethyl-3,4 : 6,7-dibenzomorphan.

Acknowledgement

The authors are thankful to the Head, Department of Chemistry, University of Rajasthan, Jaipur and one of the authors (R.S.) is thankful to C.S.I.R. for financial assistance.

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On the Reported Preparation of Co(III) Nitrate in Solution.

In the June, 1977 issue of the *J. Indian Chem. Soc.*, vol. 54, p. 579, U. N. Pandey has stated to have prepared Co(III) nitrate solution by simply aerating an aqueous solution of Co(II) nitrate. This appears highly improbable since the oxidation of Co(II)aq to the Co(III)aq ion is very unfavourable, its oxidation potential being − 1.84 volts. In fact, such oxidation in aqueous solution can be effected only electrolytically or by ozone in perchloric acid media. In aqueous solution the Co(III)aq species is quite unstable and it decomposes with evolution of oxygen forming Co(II)aq ion with a half-life of *ca.* 1 month at 0°C (the reaction is appreciably fast at room temperature). This makes one doubtful about the authenticity of the Co(III) complexes prepared by Pandey using his so-called Co(III) nitrate as the starting material.

D. Banerjea

ERRATUM

In the paper on 'A Three Term-Empirical Equation for Low-Temperature Thermal Conductivity of Solids' published on page 363 of the April 1977 issue of J. I. C. S, please *read* K. M. Jha, M. L. Thakur, S.P. Jha and S.R. Pandit *in place of* K. M. Jha, M. L. Thakur and S. P. Jha. The omission is regretted.

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Thermodynamic Stability Constants of 1-Naphthohydroxamic Acid with Copper (II), Zinc (II), Nickel (II) and Manganese (II)

Y. K. AGRAWAL* and (Miss) A. MUDALIAR

Department of Chemistry, Government Science College, Satna (M.P.), India

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The thermodynamic metal ligand stability constants of 2-naphthohydroxamic acid (2-NHA) with Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+} at 25° and 35° have been determined by pH titration technique. The order of stability found is $Cu^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$. The thermodynamic parameter were discussed.

THE analytical potentiality of 2-naphthohydroxamic acid is discussed by Vass and Yoe[1]. The data on proton ligand and metal ligand stability constants will add to better understanding for its versality in inorganic and organic analysis. A review of literature reveals that no data is available on metal ligand stability constants of 1-naphthohydroxamic acid (1-NHA). In the present communication the thermodynamic proton ligand and metal ligand stability constants of 1-NHA are described.

Experimental

Chemicals

All the chemicals used were of AnalaR and G.R. grades of B.D.H. and E. Merck, respectively.

Reagent and Apparatus

Carbonate free potassium hydroxide was prepared by the method of Vogel[2]. The metal perchlorates were prepared by treating excess of carbonates with perchloric acid and concentration of metal ions in solutions were determined volumetrically[3].

A Beckman digital pH meter equipped with glass and calomel electrode was used for pH metric measurements.

Procedure

The details of procedure and calculation for proton ligand and metal ligand stability constants were described elsewhere[4–6].

Results and Discussion

The thermodynamic proton ligand and metal ligand stability constants for Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+} with 1-NHA are summarised in Table 1. The mole ratio of metal to 1-NHA was kept 1 : 10 in

TABLE 1—THERMODYNAMIC METAL LIGAND STABILITY CONSTANTS OF 1-NAPHTHO HYDROXAMIC ACID WITH DIVALENT METAL IONS IN AQUEOUS MEDIUM

Metal ion		log K_1	log K_2	log K_1K_2
Mn^{2+}	25°	3.50	2.30	5.80
	35°	3.30	2.09	5.39
Ni^{2+}	25°	4.65	3.85	8.50
	35°	4.44	3.66	8.10
Zn^{2+}	25°	5.05	3.90	8.95
	35°	4.85	3.70	8.55
Cu^{2+}	25°	5.91	4.60	10.51
	35°	5.70	4.42	10.12
H^+	25°	7.77	—	—
	35°	7.50	—	—

TABLE 2—THERMODYNAMIC PARAMETERS FOR DIVALENT 1-NAPHTHOHYDROXAMIC ACID COMPLEXES

Metal ion	Thermo-dynamic parameter	Temp.	log K_1	log K_2	log K_1K_2
Mn^{2+}	$-\Delta G°$	25°	4.78	3.14	7.91
		35°	4.50	2.85	7.36
	$-\Delta H°$	—	8.40	8.80	17.20
	$-\Delta S°$	25°	12.14	15.63	31.16
		35°	12.65	19.30	31.92
Ni^{2+}	$-\Delta G°$	25°	6.35	5.26	11.60
		35°	6.26	5.16	11.43
	$-\Delta H°$	—	8.80	8.00	16.80
	$-\Delta S°$	25°	4.86	9.19	14.09
		35°	8.24	9.21	14.18
Zn^{2+}	$-\Delta G°$	25°	6.89	5.32	12.22
		35°	6.94	5.22	12.06
	$-\Delta H°$	—	8.40	8.40	16.80
	$-\Delta S°$	25°	5.06	10.33	15.36
		35°	5.06	10.32	15.38
Cu^{2+}	$-\Delta G°$	25°	8.07	6.28	14.35
		35°	8.04	6.24	14.28
	$-\Delta H°$	—	8.80	7.60	16.10
	$-\Delta S°$	25°	2.45	4.43	5.87
		35°	2.47	4.11	6.55

$-\Delta G°$ and $-\Delta H°$ are in Kcal $mole^{-1}$ and $-\Delta S°$ Cal.$mol^{-1}deg^{-1}$

* Present Address to whom correspondence should be made.—Dr. Y. K. Agrawal, Health Physics Division, B.A.R.C., Bombay-400085.

order to fulfil the maximum co-ordination number of metal ion. The maximum $\bar{n}$ value for all the complexes was 2, indicating a formation of 1 : 1 and 1 : 2 complexes. The thermodynamic parameters are given in Table 2

The normal order of stability shown by Maley and Mellar[7] and later Irving and Williams[8] for divalent transition metal ions as

$$Mn^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

The stability constants of 1-NHA follows the order

$$Mn^{2} < Ni^{2+} < Zn^{2+} < Cu^{2+}$$

The plot of log K_1 vs the atomic number and ΔG° have the same order of stability. Beyond manganese the constants increase with increasing atomic number reaching to a maximum with $3d^{8}$ [Cu(II)]. A decrease is observed with $3d^{10}$ [Zn(II)] as follows.

$$Mn(II) < Ni(II) < Cu(II) > [Zn(II)].$$

The stability of copper complexes are much higher than can be expected from its ionic radius or electronegativity[9] The extra stability of copper(II) complexes being square planer has been attributed to Jahn-Teller stabilization[10]. The log K_1 values plotted against the respective overall ionisation potentials of Cu(II), Zn(II), Ni(II) and Mn(II), (Fig. 1), to see the effect of electron affinity of the metal ions on the stability of the complexes they formed. A straight line obtained (Fig. 1), shows that the stability of the first complex (log K_1) formed was *directly proportional to central metal ion*. The point correspond to Cu(II) complex is above the straight line shows that the copper possesses a higher degree of stability.

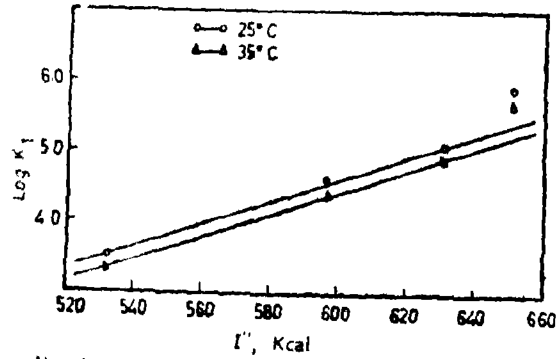


Fig. 1. Variation of Stability Constants with ionisation potential of metal ions

Acknowledgement

The authors are indebted to Prof. A. S. Kapur, Head, Department of Chemistry for necessary facilities. They are grateful to Prof. S. C. Bhattacharyya and Prof A. B. Biswas of IIT, and Shri S. D. Soman, Head, Health Physics Division for constant encouragement and helpful discussion.

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Chelating Tendencies of 8-Azaguanine

RAM NAYAN and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211002

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Stepwise formation constants of 8-azaguanine (AGN) chelates with the metal ions, Be(II), Al(III), Cr(III), Ni(II), Cu(II), Pb(II) and UO_2(VI) have been evaluated at various ionic strengths employing pH-metric technique at 30° in an aqueous media. Thermodynamic values of the formation constants were obtained by extrapolation to zero ionic strength. The stepwise thermodynamic equilibrium constants are : $K^H_1 = 10^{10.23}$, $K^H_2 = 10^{6.45}$ for H^+; and $K_1 = 10^{7.93}$, $K_2 = 10^{6.40}$ for Be(II); $K_1 = 10^{10.18}$, $K_2 = 10^{8.06}$, $K_3 = 10^{6.36}$ for Al(III); $K_1 = 10^{9.04}$, $K_2 = 10^{6.86}$ for Cr(III); $K_1 = 10^{9.44}$ for Ni(II); $K_1 = 10^{12.10}$ for Cu(II); $K_1 = 10^{6.70}$ for Pb(II); and $K_1 = 10^{10.18}$ for UO_2(VI) systems.

8-Azaguanine is structurally related to the purine, adenine, thioguanine, 6-mercaptopurine etc., which are less effective as anticancer agents than AGN. The stabilities of its metal chelates are also higher, which have been discussed.

INVESTIGATIONS on the chelation reactions of the anticancer compounds, folic acid[1], riboflavine[1], adenine[2], and thioguanine[3], and the carcinogenic compound, 1-amino-2-naphthol[3] have already been reported, and their chelating properties, like mode of reactivity and the order of stability constants etc. have been discussed in the light of their anticancer activities. 8-Azaguanine is structurally related to ADN and TGN and is comparatively more effective, but no work appears to have been done on its chelating tendencies. Thus, expecting some relationship between the chelating properties and the anticancer activities, the complexation equilibria of AGN with the carcinogenic metal ions, Be(II), Al(III), Cr(III), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), UO_2(VI), and the biologically important metal, ions Mn(II), Ca(II), Mg(II) have been studied. The experiments were carried out in aqueous media adopting the Bjerrum-Calvin pH-metric technique as used in earlier publications[1-3].

Experimental

Materials

Metal nitrate solutions were prepared using aluminium(III), chromium(III), manganese (II), cobalt(II), nickel(II), copper(II), lead(II), uranyl(VI) nitrates; beryllium(II), calcium(II) and magnesium(II) carbonates; and zinc(II) oxide (all BDH AnalaR). Nitrates were dissolved in water and carbonates and oxide were dissolved in known amounts of nitric acid. Metal contents were estimated by usual methods.

1·0M KNO_3 solution was prepared by direct weighing.

0·1016N solution of KOH (BDH AnalaR), was prepared for the titration.

AGN (Koch-Light) was dissolved in known amount of KOH, the final concentration of alkali being 0·01M.

* To whom all correspondence may be made.

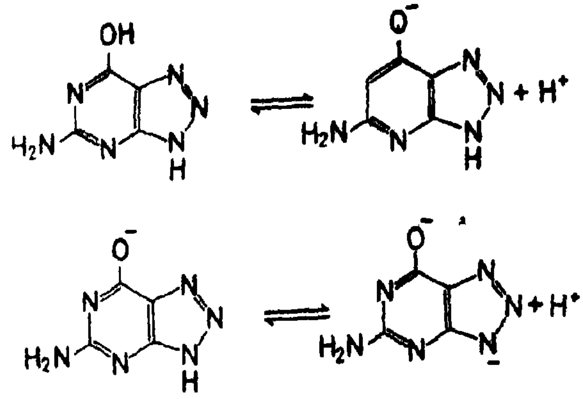
Procedure

The experiments were carried out in aqueous media at 30° employing a Leeds and Northrup pH-meter with a glass-calomel electrode assembly. The titration mixtures : (i) acid HNO_3; (ii) 0·001M AGN + mixture (i); (iii) 0·0002M metal nitrate + mixture, (ii) were titrated with the alkali keeping the total volume 50 ml. The ionic strengths were 0·01, 0·05, and 0·10M (KNO_3) as described earlier. From the experimental data, volume of alkali vs. pH, titration curves were plotted and the average number of protons attached per ligand ($\bar{n}_A$), average number of ligands attached per metal ion ($\bar{n}$), and the free ligand exponent (pL) were calculated at different pH. Formation curves of the proton-ligand system (curves of pH vs $\bar{n}_A$) and the metal-ligand systems (curves of $\bar{n}$ vs pL) were plotted and the equilibrium constants were evaluated employing the computational methods. The thermodynamic constants were obtained by extrapolating $\sqrt{\mu}$ to zero.

Results and Discussion

The titration curves of the acid and the ligand systems show that AGN contains two acidic groups which dissociate in steps like TGN. However there is no information on the protonation of the 2-amino group under the experimental conditions (between pH 3·0 and 11·0). The dissociation of the protons of ligand is shown (see next page).

The ligand solution in the absence of metal ions became turbid below pH 6·7 if it is kept for some time possibly due to the precipitation of the neutral H_2L species. This could be avoided by using freshly prepared solutions and by completing the titrations in as short a time as possible. However, it was not necessary for the studies of equilibria of chelation reactions below pH 5·0, since below this pH the ligand did not dissociate (it remains as H_2L) and the solution was perfectly clear. Thus the chelate



formation functions below pH 5·0 could be calculated using the acid and the complex curves instead of ligand and the chelate curves.

The formation curves of the protonation system show that the equilibria, $H_2L \rightleftharpoons HL^- + H^+$ and $HL^- \rightleftharpoons L^{2-} + H^+$ independently exist in the pH range between 5·0 and 8·1, and 8·3 and above respectively. The values of the formation constants for these reactions are given in table I. Protonation constant thus obtained for the amino group is consistent with those for ADN and TGN indicating a close structural relationship.

Chelate formation curves could be obtained only for Be(II), Al(III), Cr(III), Ni(II), Cu(II), UO_2(VI), and Pb(II) (Figs. are omitted), and the stability constants are given in table I. The thermodynamic values of the formation constants have been obtained extrapolating to zero ionic strength.

7·6 and 9·8, and only 1 : 1 species is formed in solution below pH 7·6.

A parallel behaviour of a number of complex species formation and the precipitation of the complexing mixture were observed for Be(II), Al(III), Cr(III) chelates with ADN[2] and TGN[3] and Ni(II)-chelate with ADN[1]. 1 : 1, 1 : 2 metal to ligand species of Cr(III) and 1 : 1 species of Ni(II) are formed in solution. The precipitation for Cr(III)-ADN[2], Cr(III)-TGN[3] and Ni(II)-ADN[2] respectively was observed at pH 7·1, 7·5, 8·1.

The maximum $\bar{n}$ values calculated for Cu(II)- and UO_2(VI)-AGN systems are 0·8 and 1·0 respectively before the precipitation of the complex solutions which occurred at pH 4·6 and 6·0 respectively. No such precipitation reaction was observed in ADN chelates with these metal ions. But in the UO_2(VI)-TGN complex mixture turbidity appeared at pH 6·6

TABLE I—FORMATION CONSTANTS OF AGN METAL-CHELATES (30°)

Ionic strength	log K_n*	H^+	Be(II)	Al(III)	Cr(III)	Ni(II)	Cu(II)	Pb(II)	UO_2(VI)
0.10	log K_1	9.90	7.53	9.68	8.63	7.19	10.67	6.24	9.41
	log K_2	6.45	5.80	7.50	6.40	...	...	...	...
	log K_3	...	...	5.90	...	...	...	...	...
0.05	log K_1	9.93	7.56	9.82	8.75	7.56	11.03	6.36	9.63
	log K_2	6.45	5.96	7.67	6.50	...	...	...	...
	log K_3	...	...	6.00	...	...	...	...	...
0.01	log K_1	10.13	7.80	10.00	8.90	7.80	11.63	6.55	9.90
	log K_2	6.45	6.20	7.85	6.70	...	...	...	...
	log K_3	...	...	6.15	...	...	...	...	...
→ 0	log K_1	10.23	7.93	10.18	9.04	8.44	12.10	6.70	10.13
	log K_2	6.45	6.40	8.06	6.86	...	...	...	...
	log K_3	...	.	6.26	...	...	...	...	...

* Range of standard deviation is between ±0·02 and ±0·04.

Be(II) and Al(III) form 1 : 1, 1 : 2 and 1 : 1, 1 : 2, 1 : 3 species respectively in solution. Precipitation was observed above pH 7·0 in the Cr(III) system, and only 1 : 1, 1 : 2 metal to ligand species could be determined in solution. In Ni(II)-AGN system thick white precipitate appeared between the pH where the solution permitted calculation of the formation constant of only 1 : 1 metal to ligand species. In the metal-chelate system of Pb(II) with ADN and TGN the precipitations were observed from the pH of complex formation, but in the present system it was possible to evaluate the formation constants

of 1 : 1 species. The turbidity appeared at $pH \approx 6{\cdot}9$.

The Mn(II), Co(II) and Zn(II) chelate systems precipitated at $pH \approx 7{\cdot}55$, 6·6 and 6·4 respectively, and the formation functions could not be evaluated. Ca(II) and Mg(II) did not show any tendency of chelate formation with AGN. Thus the chelation reactions of AGN appears quite similar to ADN and TGN with the metal ions chosen for the study.

Since, in the cancer cell the abnormal cell growth may be due to the complexation of the abnormal or the carcinogenic metal ions with the enzyme of nucleic acid systems and the anticancer drugs may check the carcinogenesis binding the abnormal metal ions or the nucleic acids via transition metal ions[4-8], the existence of the Ni(II), Be(II) and Al(III) AGN chelate equilibria at biological pH 7·3 shows that AGN can deactivate the carcinogenesis, binding the abnormal metal ions or the nucleic acids. Anticancer effects of AGN in the carcinogenesis due to the metal ions, Cu(II), UO_2(VI), Pb(II), Cr(III), and Co(II) is possible if their preicipitate remains in the form of complex species with AGN.

The order of stabilities of AGN chelates is as under :

Cu(II) > Al(III) > UO_2(VI) > Cr(III) > Ni(II) > Be(II) > Pb(II)

Comparing the stabilities of purine and its derivatives, e.g. purine (PRN), TGN, ADN, 6-marcaptopurine (6 MP) it appears that :

TGN > AGN > ADN > PRN (for Be(II), Al(III), Cr(III) and UO_2(VI) chelates)

AGN > TGN > ADN > 6 MP > PRN (for (Ni(II) chelate)

AGN > ADN > PRN (for Cu(II) chelates)

The above relations of stability constants may explain the effects of AGN as a strong anticancer agent.

Acknowledgement

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Polarographic and Infrared Studies on the Complexes of Cobalt Ammines with Schiff's Bases Derived from Salicylaldehyde, Vanillin and Amino Acids

WAHID U. MALIK[a], RAMESH BEMBI[b] and (MISS) SUSHILA

Department of Chemistry, University of Roorkee, Roorkee

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The interaction of chloropentaammine or *cis*chloroaquo tetraamine cobalt (III) chloride with Schiff's bases (derived from the condensation of salicylaldehyde with glycine (S-Gly), Aspartic acid (S-A) and Glutamic acid (S-G), and *o*-vanillin with glycine (V-Gly), Aspartic acid (V-A) and Glutamic acid (V-G) has been studied polarographically in aqueous medium and the composition of these more stable and brown coloured complexes has been established by chemical analysis, equivalent conductance, infrared spectra and polarographic data. The polarographic reduction of these complexes is found to be diffusion controlled but irreversible in nature.

EXTENSIVE studies[1-5] have been carried out on the metal complexes of Schiff's base derived from salicylaldehyde, vanillin and amino acids. These complexes provide valuable information, since they form intermediates in biological transamination[6,7] reactions and form simple models for the complicated metal-pyridoxal-amino acid systems. However, little attention has been paid to the substitution reactions in metal complexes involving Schiff's bases. Studies have, therefore, been carried out polarographically on the direct substitution of some Schiff's bases, derived from amino acids, in cobalt(III)-ammine complexes.

Maerials and Methods

The Schiff's bases were prepared by the method of Dietrich *et al.*[8] from salicylaldehyde or vanillin and amino acids. Salicylaldehyde was purified by distillation prior to use. Glycine, Aspartic acid, Glutamic acid and vanillin were A.R. grade (BDH) reagents. *cis*chloropentaamminecobalt(III) chloride and *cis*-chloroaquo tetraamminecobalt(III) chloride were prepared[9,10] from cobalt chloride.

The Schiff's base substituted cobalt(III) penta and tetraammines were prepared by the following method :

0·01 mole of the Schiff's base was added to 200 ml of a solution containing (0·01 mole) of chloropentaammine or *cis*chloroaquotetraamminecobalt(III) chloride. The mixture was gradually heated to 60° and maintained at this temperature for about 1 hr. when it turned brown. This solution was concentrated to about 50 ml under reduced pressure (below 40 mm of Hg) at 60°. It was then cooled to about 10° and a few drops of ice cold hydrochloric acid added. The solution was shaken vigorously and allowed to stand for about 1/2 hr in an ice bath when brown crystals of the Schiff's base substituted complex were obtained. These were filtered off, washed with alcohol and recrystallised from a minimum quantity of water using ice-cold hydrochloric acid and alcohol. The recrystallised product was washed with alcohol, then acetone and dried in vacuum over anhydrous calcium chloride. The complexes were prepared using Schiff's bases derived from the condensation of salicylaldehyde with glycine (S-Gly), Aspartic acid (S-A) and Glutamic acid (S-G) and *o*-vanillin with glycine (V-Gly), Aspartic acid (V-A) and Glutamic acid (V-G) respectively.

Polarograms were recorded with a Cambridge pen recording polarograph using a d.m.e. of $m^{2/3}t^{1/6}$ = 3·75 $mg^{2/3} sec^{-1/2}$. The solutions were held at 60° for 1hr and allowed to equilibrate at 30° for 1/2 hr. The requisite amount of supporting electrolyte was then added and the solutions deaerated by bubbling purified nitrogen for about 10 min before recording the polarograms. All measurements were carried out at 30±0·1°. The equivalent conductance values of the complexes were determined using a Toshniwal conductivity bridge (type CL01/01A).

The infrared spectra of the complexes were recorded in KBr discs using a Beckmann IR 20 spectrophotometer. The complexes were decomposed by boiling with hydrochloric acid and cobalt estimated gravimetrically[11,12]. Chloride ions outside the coordination sphere were estimated[12] by precipitating with $AgNO_3$ as AgCl. Results of carbon and nitrogen estimation were obtained from CDRI, Lucknow.

Results and Discussion

The interaction of chloropentaamminecobalt(III) chloride(A) with different Schiff's bases studied

[a] Present address : Bundelkhand University, Jhansi (U.P.).

[b] To whom all correspondence may be addressed.

resulted in the substitution of the coordinated chloride ion to give the Schiff's base substituted pentaamminecobalt(III) complex. In these cases the Schiff's base functions as a monodentate ligand.

Similarly, interaction of cischloroaquo tetraamminecobalt(III) chloride (B) with the above mentioned Schiff's bases, resulted in the substitution of coordinated chloride and water to give the Schiff's base substituted tetraamminocobalt(III) complex. Here the Schiff's bases act as bidentate ligands.

The resulting brown coloured, soluble complexes were studied polarographically. The limiting current for each system was found to be diffusion controlled as evidenced by linear plots of i_d vs. $h_{eff}^{1/2}$. Plots of $\log i/(i_d-i)$ vs $E_{d.e.}$ show that the waves are irreversible. The $E_{\frac{1}{2}}$ of the cobalt(III)-ammine complexes show shift towards more negative potentials in increasing concentration of the Schiff's bases. Since the waves are irreversible, the classical method of Lingane[13] could not be used for studying the complex ion formation. Therefore, the method recommended by Tamamushi and Tanaka[14] was employed. According to them :

$$\frac{\Delta E_{1/2}}{\Delta \log C_x} = -j\,\frac{0{\cdot}06014}{n\alpha} \quad \ldots (1)$$

where α is the fraction of the total applied potential that favours the forward reaction and 'j' is the number of ligands bound to the metal. The value of $n\alpha$ is given by the equation :

$$E_{3/4}-E_{1/4} = \frac{-0{\cdot}0574}{n\alpha} \quad \ldots (2)$$

The value of $\Delta E_{1/2}/\Delta \log C_x$ is determined from the slope of the plots of $\log C_x$ vs $E_{1/2}$ where C_x is the concentration of the Schiff's base. The value of j thus obtained works out to be approximately 1·0 in all the cases showing thereby that one mole of Schiff's base combines with 1 mole of the metal ion. It may therefore be concluded that 1 : 1 interaction takes place between A or B and the Schiff's bases. The stability constants of the Schiff's base complexes were also calculated from the polarographic data and are given in Table 1.

TABLE 1—POLAROGRAPHIC DATA AND STABILITY CONSTANTS OF THE SCHIFF'S BASE COMPLEXES

Complex of	j	Stability constant log K
Pentaamine cobalt(III) with		
1. S-Gly	1.2	0.63
2. S-A	1.1	2.68
3. S-G	1.3	1.63
4. V-Gly	1.1	3.38
5. V-A	1.0	2.67
6. V-G	1.3	1.69
Tetraammine cobalt(III) with		
7. S-Gly	1.0	4.61
8. S-A	1.2	3.58
9. S-G	1.1	3.05
10. V-Gly	1.1	3.65
11. V-A	1.2	3.67
12. V-G	1.0	2.53

Chemical analysis of these complexes shows that one mole each of A or B and the Schiff's base react to give the substitution product. The equivalent conductance values are in accord with formation of monovalent complex-ions (except with (V-Gly) which gives a divalent moiety) in the case of tetraammines and bivalent complex-ions is the case of pentaammines.

The important infrared spectral characteristics of these complexes are given in Table 2. The infrared

TABLE 2—INFRARED SPECTRAL CHARACTERISTICS OF SCHIFF'S BASE COMPLEXES (cm^{-1})

Complex	$\nu(NH_3)$	Asym. $\nu(CO\bar{O})$	Sym. $\nu(CO\bar{O})$	$\nu(C=N)$
1. $[Co(NH_3)_5(S\text{-}Gly)]Cl_2$	3140	1620	1430	1640
2. $[Co(NH_3)_5(S\text{-}A)]Cl_2$	3160	1600	1400	1620
3. $[Co(NH_3)_5(S\text{-}G)]Cl_2$	3300 3160	1600	1400	1620
4. $[Co(NH_3)_5(V\text{-}Gly)]Cl_2$	3160	1600	1400	1630
5. $[Co(NH_3)_5(V\text{-}A)]Cl_2$	3160	1600	1400	1640
6. $[Co(NH_3)_5(V\text{-}G)]Cl_2$	3400	1600	1400	1630
7. $[Co(NH_3)_4(S\text{-}Gly)]Cl_2$	3360 3160	1600	1400	1620
8. $[Co(NH_3)_4(S\text{-}A)]Cl$	3400 3130	1600	1400	1630
9. $[Co(NH_3)_4(S\text{-}G)]Cl$	3300 3120	1600	1380	1640
10. $[Co(NH_3)_4(V\text{-}Gly)]Cl_2$	3300 3200	1600	1400	1620
11. $[Co(NH_3)_4(V\text{-}A)]Cl$	3280 3120	1620	1390	1630
12. $[Co(NH_3)_4(V\text{-}G)]Cl$	3400 3120	1600	1400	1640

spectra of Schiff's base substituted chloropentaammine cobalt(III) chloride shows binding of the Schiff's base through the carboxylic group. This conclusion is drawn from the fact that more pronounced bands around 1400 cm^{-1} and 1600 cm^{-1} appear, which may be assigned to the symmetric stretching of the coordinated carboxylic group and overlap of the asymmetric stretching of the carboxylic group and ammonia deformation mode respectively. The presence of these two bands coupled with the absence of the absorption around 1700 cm^{-1} (due to normal carbonyl absorption of the -COOH group of the Schiff's base) provides evidence to confirm the coordination of the Schiff's base to cobalt through the carboxylic group[15].

The infrared spectra of the tetraammines shows binding of the Schiff's base through the carboxylic groups in the case of (S-A), (S-G), (V-A) and (V-G) while in the case of (S-Gly) and (V-Gly), the binding is through the carboxylic group and the nitrogen of the C = N group. The infrared spectra shows bands

around 1600 and 1400 cm^{-1} corresponding to symmetric stretching of the coordinated carboxylic group and overlap of the asymmetric stretching of the carboxylic group and ammonia deformation mode respectively in all the complexes. In the cases of (S-A), (S-G), (V-A) and (V-G) and their tetraammine cobalt complexes, the C = N stretching frequency appears at the same frequency in the region 1640–1620 cm^{-1}. Since there is no shift in C = N frequency on coordination of the Schiff's base, it is evident that the nitrogen of this group is not involved in coordination in these complexes. In the case of (S-Gly) and (V-Gly), the C = N stretching frequency appears at 1640 cm^{-1} and 1630 cm^{-1} which shows shift to 1620 cm^{-1} in their tetraammine complexes, thereby showing binding through nitrogen of the C = N group[16]

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Thiazolidinones-Part XIII
Synthesis of 2-Aryl-3-β-Aryloxyethyl-4-Thiazolidinones and their 1,1-Dioxides

P. B. PATEL and J. J. TRIVEDI*

Bapulal H. Vakil, Chemical Research Laboratory, Smt. B. C. J. Science College, Cambay, Dist. Kaira

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Several 2-aryl-3-β-aryloxyethyl-4-thiazolidinones have been prepared by condensing Schiff bases, from β-aryloxyethylamines and aryl aldehydes, with thioglycolic acid. These on oxidation, with potassium permanganate, gave the corresponding 1,1-dioxides. Some of these compounds exhibited antiinflammatory activity.

2,3-DISUBSTITUTED thiazolidinones are reported to exhibit anaesthetic[12], anticonvulsant[13] and hypnotic[3] activities. Surrey and Cutler[4] prepared 2-aryl-3-(2-methoxyethyl)-4-thiazolidinones and their dioxides and found them to be active as psychomotor stimulants and anticonvulsants. In light of the varied physiological activities such as antihistaminic[7], general adrenolytic[6], stimulation of autonomic ganglia[9] and of skeletal muscle[5] and local anaesthetic[10] activity shown by aryloxyalkyl amines, it was considered of interest to study biological activity of thiazolidinones containing aryloxyalkyl group. With this in view 2-aryl-3-β-aryloxyethyl-4-thiazolidinones have been prepared by the condensation of Schiff bases, from aromatic aldehydes and β-aryloxyethylamines, with thioglycolic acid. These thiazolidinones, on oxidation with potassium permanganate gave the corresponding 1,1-dioxides.

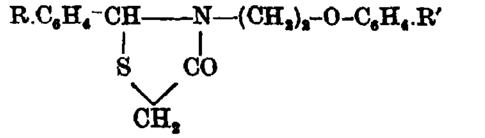
Experimental

β-Aryloxyethyl bromides were prepared as described in literature[8]. The required β-aryloxyethyl amines were prepared from β-aryloxyethyl bromides by Delepine reaction[11].

2-Aryl-3-β-Aryloxyethyl-4-Thiazolidinones[1] :

A mixture of aryl aldehyde (0·02 mole) and β-aryloxyethylamine (0·02 mole) in dry benzene (25 ml) was refluxed under a Dean and Stark water separator. After the theoretical quantity of water was separated (4–5 hrs), thioglycolic acid (2·0 g) was added and refluxing was continued, till no more water separated. The residue after removal of benzene was taken up in ether, washed successively with sodium bicarbonate solution, dilute HCl (1 : 1) and 10% sodium bisulphite solution to remove the acid formed during the reaction, β-aryloxyethyl amine and the unused aldehyde respectively and finally with water. The solvent

TABLE 1—2-ARYL-3-β-ARYLOXYETHYL-4-THIAZOLIDINONES



No.	R	R′	M.P. °C	Molecular Formula	Percent Sulphur		Pharmacological Results
					Found	Required	Inhibition (%) in Careeggenin edema (Rats) dose 100 mg/kg
1.	H	H	90–92	$C_{17}H_{17}O_2NS$	10.50	10.70	—
2.	,,	o-CH_3	59–62	$C_{18}H_{19}O_2NS$	10.00	10.20	—
3.	,,	p-CH_3	90–92	$C_{18}H_{19}O_2NS$	10.10	10.20	—
4.	,,	o-Cl	105–107	$C_{17}H_{16}O_2NClS$	9.40	9.60	73
5.	,,	p-Cl	121–122	$C_{17}H_{16}O_2NClS$	9.70	9.60	—
6.	,,	2,4-$(Cl)_2$	101	$C_{17}H_{15}O_2NCl_2S$	8.60	8.70	—
7.	,,	2,5-$(Cl)_2$	126	$C_{17}H_{15}O_2NCl_2S$	8.50	8.70	53
8.	,,	2,4-$(CH_3)_2$	108	$C_{19}H_{21}O_2NS$	9.60	9.80	—
9.	,,	2-CH_3-4-Cl	106–108	$C_{18}H_{18}O_2NClS$	9.00	9.20	—
10.	,,	2-CH_3-5-Cl	105	$C_{18}H_{18}O_2NClS$	9.10	9.20	66

* For correspondence — M. G. Science Institute, Ahmedabad-380009.

was evaporated and the residue crystallised from alcohol (Yield about 70–80%). Compounds prepared in this way are shown in Table 1.

1,1-Dioxides[2]:

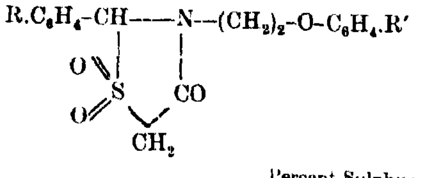
A solution of $KMnO_4$ (0·65 g. in water (15 ml) was added with stirring to a solution of 2-aryl-3-β-

Table 1 (*contd*).

No.	R	R′	M.P. °C	Molecular Formula	Percent Sulphur		Pharmacological Results
					Found	Required	Inhibition (%) in Careeggenin edema (Rats) dose 100 mg/kg
11.	p-OCH_3	H	92–94	$C_{18}H_{19}O_3NS$	9.60	9.70	—
12.	,,	o-CH_3	55–57	$C_{19}H_{21}O_3NS$	9.00	9.30	—
13.	,,	p-CH_3	88–90	$C_{19}H_{21}O_3NS$	9.10	9.30	—
14.	,,	o-Cl	76	$C_{18}H_{18}O_3NClS$	8.50	8.80	73
15.	,,	p-Cl	95–96	$C_{18}H_{18}O_3NClS$	8.60	8.80	57
16.	,,	2,4-$(Cl)_2$	120	$C_{18}H_{17}O_3NCl_2S$	7.80	8.00	—
17.	,,	2,5-(Cl)2	114–116	$C_{18}H_{17}O_3NCl_2S$	7.80	8.00	—
18.	,,	2,4-$(CH_3)_2$	92	$C_{20}H_{23}O_3NS$	8.80	9.00	—
19.	,,	2-CH_3-4-Cl	90–91	$C_{19}H_{20}O_3NClS$	8.40	8.50	67
20.	,,	2-CH_3-5-Cl	100–101	$C_{19}H_{20}O_3NClS$	8.60	8.50	—
21.	o-Cl	H	55–58	$C_{17}H_{16}O_2NClS$	9.40	9.60	—
22.	,,	o-CH_3	89–90	$C_{18}H_{18}O_2NClS$	9.00	9.20	50
23.	,,	p-CH_3	113–15	$C_{18}H_{18}O_2NClS$	9.10	9.20	—
24.	,,	o-Cl	105–106	$C_{17}H_{15}O_2NCl_2S$	8.90	8.70	57
25.	,,	p-Cl	85–87	$C_{17}H_{15}O_2NCl_2S$	8.60	8.70	50
26.	,,	2,4-$(Cl)_2$	90–91	$C_{17}H_{14}O_2NCl_2S$	7.80	8.00	67
27.	,,	2,5-$(Cl)_2$	161–162	$C_{17}H_{14}O_2NCl_3S$	8.10	8.00	—
28.	,,	2,4-$(CH_3)_2$	95	$C_{19}H_{20}O_2NClS$	8.60	8.80	—
29.	,,	2-CH_3-4-Cl	116–117	$C_{18}H_{17}O_2NCl_2S$	8.20	8.40	78
30.	,,	2-CH_3-5-Cl	140	$C_{18}H_{17}O_2NCl_2S$	8.30	8.40	—
31.	p-Cl	H	78–80	$C_{17}H_{16}O_2NClS$	9.40	9.60	—
32.	,,	o-CH_3	118–119	$C_{18}H_{18}O_2NClS$	9.00	9.20	—
33.	,,	p-CH_3	124	$C_{18}H_{18}O_2NClS$	9.00	9.20	—
34.	,,	o-Cl	135–136	$C_{17}H_{15}O_2NCl_2S$	8.60	8.70	50
35.	,,	p-Cl	114–116	$C_{17}H_{15}O_2NCl_2S$	8.50	8.70	55
36.	,,	2,4-$(Cl)_2$	102–104	$C_{17}H_{14}O_2NCl_3S$	7.80	8.00	—
37.	,,	2,5-$(Cl)_2$	155–157	$C_{17}H_{14}O_2NCl_3S$	7.90	8.00	73
38.	,,	2,4-$(CH_3)_2$	92	$C_{19}H_{20}O_2NClS$	8.60	8.80	89
39.	,,	2-CH_3-4-Cl	106	$C_{18}H_{17}O_2NCl_2S$	8.20	8.40	—
40.	,,	2-CH_3-5-Cl	130–131	$C_{18}H_{17}O_2NCl_2S$	8.20	8.40	—
41.	2,4-$(Cl)_2$	H	90	$C_{17}H_{15}O_2NCl_2S$	8.60	8.70	70
42.	,,	o-CH_3	118	$C_{18}H_{17}O_2NCl_2S$	8.20	8.40	66
43.	,,	p-CH_3	110–114	$C_{18}H_{17}O_2NCl_2S$	8.20	8.40	78
44.	,,	o-Cl	102–104	$C_{17}H_{14}O_2NCl_3S$	7.90	8.00	40
45.	,,	p-Cl	114–116	$C_{17}H_{14}O_2NCl_3S$	7.80	8.00	45
46.	,,	2,4-$(Cl)_2$	165	$C_{17}H_{13}O_2NCl_4S$	7.20	7.30	—
47.	,,	2,5-$(Cl)_2$	142–144	$C_{17}H_{13}O_2NCl_4S$	7.10	7.30	39
48.	,,	2,4-$(CH_3)_2$	128	$C_{19}H_{19}O_2NCl_2S$	7.90	8.10	—
49.	,,	2-CH_3-4-Cl	136	$C_{18}H_{16}O_2NCl_3S$	7.50	7.70	38
50.	,,	2-CH_3-5-Cl	120–122	$C_{18}H_{16}O_2NCl_3S$	7.50	7.70	—

(100 mg. of Phenylbutazone produced 43% inhibition of Careeggenin edema (Rats).

TABLE 2—1·1-DIOXIDES OF 2-ARYL-3-β-ARYLOXYETHYL-4-THIAZOLIDINONES



No.	R	R′	M.P. °C	Molecular Formula	Percent Sulphur		Pharmacological Results
					Found	Required	Inhibition (%) in Careeggenin edema (Rats) dose 100 mg/kg
1.	H	H	110	$C_{17}H_{17}O_4NS$	9.50	9.70	—
2.	,,	p-CH_3	120–122	$C_{18}H_{19}O_4NS$	9.00	9.30	—
3.	,,	o-Cl	138–140	$C_{17}H_{16}O_4NClS$	8.30	8.50	—
4.	,,	p-Cl	152–154	$C_{17}H_{16}O_4NClS$	8.70	8.50	—
5.	,,	2,4-$(Cl)_2$	170–171	$C_{17}H_{15}O_4NCl_2S$	7.80	8.00	—

Table 2 (*contd.*)

No.	R	R′	M.P. °C	Molecular Formula	Percent Sulphur Found	Percent Sulphur Required	Pharmacological Results: Inhibition (%) in Careeggenin edema (Rats) dose 100 mg/kg
6.	,,	2,5-$(Cl)_2$	174–176	$C_{17}H_{15}O_4NCl_2S$	7.90	8.00	52
7.	,,	2,4-$(CH_3)_2$	134	$C_{19}H_{21}O_4NS$	9.70	9.80	—
8.	,,	2-CH_3-4-Cl	153	$C_{18}H_{18}O_4NClS$	8.20	8.40	—
9.	,,	2-CH_3-5-Cl	130–132	$C_{18}H_{18}O_4NClS$	8 .30	8.40	—
10.	*p*-OCH_3	H	104–105	$C_{18}H_{19}O_5NS$	8.80	8.90	—
11.	,,	*p*-CH_3	125	$C_{19}H_{21}O_5NS$	8.40	8.50	—
12.	,,	*o*-Cl	140	$C_{18}H_{18}O_5NClS$	7.90	8.10	43
13.	,,	*p*-Cl	172–175	$C_{18}H_{18}O_5NClS$	7.90	8.10	—
14.	,,	2,4-$(Cl)_2$	144	$C_{18}H_{17}O_5NCl_2S$	7.20	7.40	—
15.	,,	2,5-$(Cl)_2$	170	$C_{18}H_{17}O_5NCl_2S$	7.60	7.40	30
16.	,,	2,4-$(CH_3)_2$	117	$C_{20}H_{23}O_5NS$	8.00	8.20	—
17.	,,	2-CH_3-4-Cl	137–140	$C_{19}H_{20}O_5NClS$	7.40	7.60	—
18.	,,	2-CH_3-5-Cl	145–147	$C_{19}H_{20}O_5NClS$	7.40	7.40	—
19.	*o*-Cl	*o*-CH_3	160–162	$C_{18}H_{18}O_4NClS$	8.20	8.40	—
20.	,,	*p*-CH_3	143–145	$C_{18}H_{08}O_4NClS$	8.30	8.40	—
21.	,,	*o*-Cl	156	$C_{17}H_{15}O_4NCl_2S$	8.20	8.00	—
22.	,,	*p*-Cl	182	$C_{17}H_{15}O_4NCl_2S$	7.90	8.00	—
23.	,,	2,4-$(Cl)_2$	186–188	$C_{17}H_{14}O_4NCl_3S$	7.20	7.40	—
24.	,,	2,5-$(Cl)_2$	180–182	$C_{17}H_{14}O_4NCl_3S$	7.10	7.40	43
25.	,,	2,4-$(CH_3)_2$	158–160	$C_{19}H_{20}O_4NClS$	7.90	8.10	—
16.	,,	2-CH_3-4-Cl	168	$C_{18}H_{17}O_4NCl_2S$	7.50	7.70	—
27.	,,	2-CH_3-5-Cl	164	$C_{18}H_{17}O_4NCl_2S$	7.50	7.70	—
28.	*p*-Cl	H	165–168	$C_{17}H_{16}O_4NClS$	8.30	8.50	—
29.	,,	*o*-CH_3	170	$C_{18}H_{18}O_4NClS$	8.30	8.40	67
30.	,,	*p*-CH_3	164–165	$C_{18}H_{18}O_4NClS$	8.20	8.40	—
31.	,,	*o*-Cl	160–162	$C_{17}H_{15}O_4NCl_2S$	8.20	8.00	—
32.	,,	*p*-Cl	184	$C_{17}H_{13}O_4NCl_2S$	7.90	8.00	—
33.	,,	2,4-$(Cl)_2$	174	$C_{17}H_{14}O_4NCl_3S$	7.50	7.40	—
34.	,,	2,5-$(Cl)_2$	209–212	$C_{17}H_{14}O_4NCl_3S$	7.20	7.40	60
35.	,,	2,4-$(CH_3)_2$	144–147	$C_{19}H_{20}O_4NClS$	7.90	8.10	—
36.	,,	2-CH_3-4-Cl	181	$C_{18}H_{17}O_4NCl_2S$	7.50	7.70	—
27.	,,	2-CH_3-5-Cl	182-184	$C_{18}H_{17}O_4NCl_2S$	7.40	7.70	—
38.	2,4-$(Cl)_2$	H	158	$C_{17}H_{15}O_4NCl_2S$	7.90	8.00	—
39.	,,	*o*-CH_3	148	$C_{18}H_{17}O_4NCl_2S$	7.50	7.70	—
40.	,,	*p*-CH_3	132	$C_{18}H_{17}O_4NCl_2S$	7.90	7.70	—
41.	,,	*o*-Cl	189	$C_{17}H_{14}O_4NCl_3S$	7.20	7.40	57
42.	,,	*p*-Cl	186–188	$C_{17}H_{14}O_4NCl_3S$	7.20	7.40	57
43.	,,	2,4-$(Cl)_2$	187–188	$C_{17}H_{13}O_4NCl_4S$	6.50	6.70	—
44.	,,	2,5$(Cl)_2$	202–204	$C_{17}H_{13}O_4NCl_4S$	6.60	6.70	48
45.	,,	2,4-$(CH_3)_2$	162–164	$C_{19}H_{19}O_4NCl_2S$	7.10	7.30	—
46.	,,	2-CH_3-4-Cl	162–164	$C_{19}H_{16}O_4NCl_3S$	7.00	7.10	—
47.	,,	2-CH_3-5-Cl	186–188	$C_{18}H_{16}O_4NCl_3S$	6.90	7.10	—

(100 mg. of Phenylbutazone produced 43% inhibition of careeggenin edema (Rats).

aryloxyethyl-4-thiazolidinones (0·002mole) in glacial acetic acid (10 ml) at 35–40°. Stirring was continued for about 30–60 mins. Sodium bisulphite solution was added to remove the excess of $KMnO_4$ and the 1,1-dioxides which separated on adding water (Yield 40–60%) were crystallised from alcohol or acetic acid. These are shown in Table 2.

Structureactivity relationship :

1. 1 : 1-dioxides are less active as compared to the parent compounds.

2. Increase in the number of chlorine atoms decreases the activity in majority of cases.

3. Replacement of one chlorine by methyl in the case of dichloro compounds increases the activity. 2,4-Dimethyl (No. 38) has the highest activity.

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Base Adduct of Bis (Chloro Acetyl Acetonato) Copper(II) with Nitrogen Donors

O. D. RAO and B. K. MOHAPATRA

Department of Chemistry, Ravenshaw College, Cuttack-3

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Three green crystalline base adduct having the general formula [Cu(Cl-ac.ac)$_2$L] where Cl-ac.ac is the chloro-acetyl acetone anion and L is nitrogen ligand like quinoline, isoquinoline and beta-picoline, have been synthesized, These were characterised on the basis of analysis, conductance, magnetic susceptibility, i.r. and electronic spectral data are presumably penta-coordinated.

BONDING of additional ligands along the axis normal to the molecular plane of planar complexes has invoked interest in recent years. Spectral evidence is available[1] for the coordination of heterocyclic bases to the planar molecule of bis-(acetyl acetonato) copper(II) and 1 : 1 adducts of this complex with 4-methyl pyridine and quinoline have been isolated[2,3], the base is lost very readily. We have been trying for the adduct formation of metal beta-diketonates with heterocyclic bases and isolated[4,5] a number of penta-coordinated adducts of zinc(II) beta-diketonates with heterocyclic amines. A quinoline adduct of bis(benzoyl acetonato) copper-(II) has been reported[6]. Stability of acetylacetonates has been partly explained on the basis of benzenoid resonance[7] and reactions characteristic of aromatic system have been carried out[8–10] on metal acetylacetonates to provide further evidence regarding aromaticity. It was, therefore, thought worthwhile to study the adduct formations of gamma-substituted beta-diketonates and as a part of this investigation a quinoline adduct of bis(nitroacetyl acetonato) copper(II) has been described[11]. This communication describes three green crystalline 1 : 1 base (quinoline, isoquinoline, beta-picoline) adducts of bis (chloroacetylacetonato) copper(II).

Experimental

Bis(chloro acetylacetonato) copper(II) was prepared by reacting a methonolic solution of the chelate with dry chlorine gas, and by cooling the reaction mixture in an ice bath. The green compound separated was filtered under suction, washed with methanol, followed by ether and dried *in vacuo*. Analysis of the compound indicated the composition [Cu(Cl-ac.ac)$_2$]. I.R. spectra provided evidence for the formation of chloro chelate.

The chelate was dissolved in the respective bases by warming till a saturated solution was obtained. The solution was cooled in ice-bath when green crystalline compounds separated out. Excess of the base was driven out by suction and by keeping in a vacuum desiccator containing paraffin.

Composition of the compounds was established by analysing metal, nitrogen and halogen. [Cu(Cl-ac.ac)$_2$L] where L is quinoline and isoquinoline requires, Cu = 19·55, N = 4·31, Cl = 10·92; Found : Cu = 19·32, 19·20; N = 4·1, 4·3; Cl = 10·65, 10·68 respectively. For L = beta-picoline, requires Cu = 21·92, N = 4·83, Cl = 12·24. Found Cu = 21·65, N = 4·58, Cl = 11·92. Conductance was measured in 0·001*M* acetone solution. Magnetic susceptibility measurement was made on solid specimen using Gouy method. I.R. spectra were recorded on nujol mulls using Unicam SP 200 and Perkin-Elmer 5100 spectrometer. Electronic spectra was recorded in 0·01*M* chloroform-base solution using Unicam SP500 spectrometer. Spectral data are recorded in Table 1.

TABLE 1

Infrared spectra (cm^{-1})

Compound	ν(C=C)	ν(C=O)	ν(C-Cl)	ν(M-O)	ν(M-N)
Cu(ac.ac)$_2$	1590	1555	—	440	—
Cu(Cl-ac.ac)$_2$	1565	1545	1090	440	—
[Cu(Cl-ac.ac)$_2$Q]	1570	1555	1090	430	320
[Cu(Cl-ac.ac)$_2$I.Q]	1575	1560	1085	425	320
[Cu(Cl-ac.ac)$_2$β-pic]	1580	1560	1090	430	325

Electronic spectra

	ν_{max}(nm)	(ε)
Cu(Cl-ac.ac)$_2$	660	100
[Cu(Cl-ac.ac)$_2$Q]	650	130
[Cu(Cl-ac.ac)$_2$I.Q]	640	125
[Cu(Cl-ac.ac)$_2$β-pic]	650	120

Q = Quinoline, I.Q. = Isoquinoline, β-pic = beta-picoline.

Results and Discussion

Analysis of the green crystalline compounds correspond to the composition [Cu(Cl-ac.ac)$_2$L] where L is quinoline, isoquinoline and beta-picoline. The low conductance values (8, 11 and 12 mhos) in acetone are indicative of the non-electrolytic nature of the complexes. Magnetic measurement show the complexes to be paramagnetic (μ_{eff} = 1·82, 1·84 and

1·78 B.M. respectively) with the presence of one unpaired electron.

Infrared spectra of the chelate, chlorochelate and the base adduct are given in Table 1. It is seen that the C–C and C–O stretching frequency of the chelate decreases to a lower frequency and the bands due to C–H stretching and bending vibrations disappear on chlorination. The extent of decrease in frequency is more in case of ν(C – C). Disappearance of bands due to ν(C–H) at 3000 cm^{-1} and δ(C–H) around 1200 cm^{-1} and appearance of a new band around 1090 cm^{-1} attributable to ν(C–Cl) provides evidence for chlorination of the chelate. The spectra of the base adduct is complicated for assignment, but most of the bands due to the base are shifted indicating bonding of the nitrogen donor ligand, the information only being obtained by the finger print technique. Concrete evidence for bonding of the base is however, obtained from the shift of ν(C – C) and ν(C – O) to higher frequency region in the base adducts and bands attributable to ν(M–O) and ν(M–N) around 430 and 320 cm^{-1} respectively in the far-infrared spectrum of the adduct. This has been further substantiated by the observation that the chloro chelate absorbs moisture when left exposed to air and forms [Cu(Cl-ac ac)$_2$.H_2O], the presence of water being identified by analysis and an absorption band at 3450 cm^{-1} in the i.r. spectrum.

Cu(ac.ac)$_2$ gives rise to high intensity band at 245 nm (ϵ = 20,000) whereas in the chlorochelate the band shifts to the longer wavelength region, i.e., 268 nm (ϵ = 11,000) as the halogenation results in the increase of pi-electron delocalisation in the ring, thereby extending conjugation.

A single broad absorption band is observed for [Cu(Cl-ac.ac)$_2$L] around 650 nm (ϵ = 130) in the visible region whereas in case of the chloro chelate the band is around 660 nm (ϵ = 100). Though the band does not shift much on coordination with the base there is an increase in the extinction coefficient. Gillard and Wilkinson[3] have studied the absorption spectra of Cu(ac.ac)$_2$ and [Cu(ac ac)$_2$.Q] in dichloromethane and reported bands at 658 nm (ϵ = 41) for the former and 650 nm (ϵ = 71) for the latter compound. Shigmatsu[12] *et al* have observed the λ_{max} for [Cu(ac.ac)$_2$.py] at 660 nm in benzene, acetone and chloroform solutions. Graddon[13] has also observed that there is an increase in the extinction coefficient of the mono adducts of copper(II) beta-diketonates without much shift in the absorption maxima.

Hence the compound under report is presumably penta-coordinated basing on its analysis, i.r. spectra and similar nature of electronic spectra. However, X-ray crystal structure study is desirable to ascertain its preferred stereochemistry, though the compound [Cu(ac.ac)$_2$.Q] has a square pyramidal structure from X-ray study.

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Studies on Hydroxamic Acids. Part VII. Preparation, Properties and Analytical Application of Thorium (IV) N-*m*-Tolyl-*m*-Nitrobenzohydroxamate

Y. K. AGRAWAL* and T. P. SHARMA**

Department of Chemistry, Government Polytechnic, Ujjain (M.P.)

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A new complex of thorium(IV) with N-*m*-tolyl-*m*-nitrobenzohydroxamic acid was prepared by reacting an aqueous solution of Th with an alcoholic solution of N-*m*-tolyl-*m*-nitrobenzohydroxamic acid at 60° and adjusting the *p*H 4-4.5. The infrared spectra and thermal analysis of the complex have been discussed. The use of N-*m*-T-NBHA for gravimetric determination of thorium is described.

IN continuation with previous work on the use of N-*m*-tolyl-*m*-nitrobenzohydroxamic acid (N-*m*-T-NBHA)[1,10] a new solid complex Th N-*m*-T-NBHA is described. The infrared spectra, DTA and TGA of N-*m*-T-NBHA thorium complex were studied. The use of N-*m*-T-NBHA as a gravimetric reagent for micro-gram determination of thorium in presence of foreign ions has been reported.

Experimental

Chemical

All chemicals used were of G.R. and AnalaR grades of E. Merck and B.D.H. respectively unless otherwise stated.

Reagents

The N-*m*-tolyl-*m*-nitrobenzohydroxamic acid was synthesised by the method described earlier[11].

The aqueous stock solution of thorium was prepared by dissolving 1·3805 g. thorium nitrate in 250 ml. of double distilled water and the final concentration was determined volumetrically[12].

Procedure

In a lite beaker, 10 ml of a 0·001*M* solution of thorium nitrate and about 500 ml water were heated at 60° on a water bath. Then 20 ml of 0·1*M* solution of N-*m*-T-NBHA in ethanol was added dropwise with constant stirring followed by 0·1*N* ammonium hydroxide until complete precipitation was obtained. The *p*H 4–4·5 was adjusted by ammonium acetate and acetic acid solution. The granular precipitate thus formed was digested for 2-3 hrs over a steam bath, filtered through a sintered glass crucible of porosity G4 and washed thoroughly with hot water and finally with 30 per cent aqueous ethanol (5 × 10 ml). The complex was purified by reprecipitation from a mixture of ethanol-water and dried at 110°.

The same procedure was used for gravimetric determination of thorium and the complex was weighed directly.

Analysis

Weighed quantity of complex was decomposed with a mixture of perchloric, sulphuric and nitric acids and the thorium content was determined volumetrically with EDTA using xynol orange as an indicator.

Thermal Analysis

Simultaneous plots of T.G. and DTA were obtained at a constant heating rate of 8°C/min on a Metler thermal analyser fitted with a 12 channel recorder. Al_2O_3 was used as a reference material for DTA.

Spectra

The infrared spectra of the reagent and thorium complex were recorded on Perkin Elmer Model 137 spectrophotometer with sodium chloride optics as KBr pellets.

Results and Discussion

The physical properties of the complex are given in Table 1. The data on gravimetric determination of thorium(IV) in presence of various foreign ions are given in Table 2 and Table 3. The DTA and TGA curves of the complex are reproduced in figure 1.

N-*m*-tolyl-*m*-nitrobenzohydroxamic N-*m*-T-NBHA, I, is a very weak acid[3] (pK_a 8·33 at 25°) and reacts

* To whom correspondence should be made at, Pharmacy Department, Faculty of Technology and Engineering, M. S. University of Baroda, Baroda (Gujarat), India.

** Department of Chemistry, Madhav Science College, Ujjain (M.P.).

TABLE 1—PHYSICAL PROPERTIES OF THE THORIUM-N-*m*-TOLYL-*m*-NITROBENZOHYDROXAMIC ACID COMPLEXES

Colour	:	Yellowish			
m.p., °C	:	210*			
pH of precipitation	:	4–4.5			
Analysis %		C	H	N	Th
Calculated	:	51.07	3.37	8.51	17.64
Found	:	51.10	3.35	8.50	17.65
DTA					
1st Exotherm	:	210°			
2nd Exotherm	:	600°			
Residue	:	ThO_2			
TGA					
Weight loss calculated	:	79.93%			
Found	:	79.56%			

* The complex is decomposed.

TABLE 2—GRAVIMETRIC DETERMINATION OF THORIUM WITH N-*m*-TOLYL-*m*-NITROBENZOHYDROXAMIC ACID

Th Taken mg	Th Found mg	Error
5.00	5.01	+0.01
5.00	5.00	±0.00
7.50	7.48	−0.02
10.00	9.98	−0.02
15.00	15.02	+0.02
15.00	15.01	+0.01

TABLE 3—SEPARATION OF THORIUM FROM OTHER METALS

Thorium Taken mg	Foreign Ions mg	Masking agent	Thorium Found mg
5.00	Ag^{+} 60	Acetate	5.00
5.00	Be^{+2} 80	Acetate	5.03
5.00	Pb^{+2} 80	Acetate	5.01
5.00	Mn^{+2} 80	Acetate	4.98
10.00	Ni^{2+} 80	Acetate+Citrate	9.98
10.00	Cu^{+2} 80	Cynide+Acetate	9.97
10.00	Zn^{+2} 80	Acetate+Cyanide	10.02
5.00	Cd^{+2} 80	EDTA	5.00
5.00	Hg^{+2} 70	Acetate+Citrate	5.03
5.00	Pd^{+2} 100	Citrate+Oxalate	4.98
5.00	Ga^{+3} 100	Acetate+Citrate	5.02
5.00	Al^{+3} 100	Acetate+Citrate	4.97
5.00	Bi^{+3} 70	Acetate+Tartrate	4.97
5.00	Sb^{+3} 80	Acetate+Tartrate	5.01
5.00	La^{+3} 80	Acetate+Citrate	4.98
5.00	Ti^{+4} 100	Acetate+Tartrate	5.00
5.00	Zr^{+4} 100	Citrate+Oxalate	5.02
5.00	V^{+5} 100	Acetate Mg-EDTA	5.02
5.00	Mo^{+6} 80	Acetate+Citrate	5.01
5.00	U^{+6} 60	Acetate+Tartrate	5.02

to around 150°–180° indicating the absence of water molecule. DTA for the complex shows two exotherms, first at 225°, a very sharp one along with loss in weight and second a broad exotherm around 400° with a further weight loss, presumably due to buring of organic matter. No evidence of melting is observed.

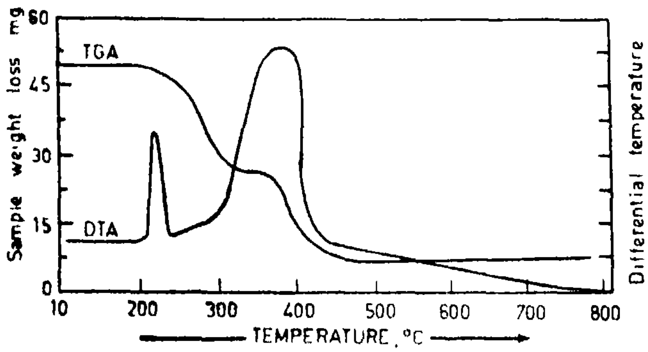
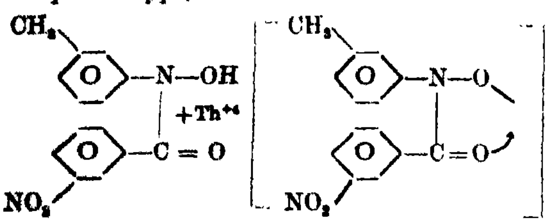


Fig. 1. DTA and TGA of Thorium (IV)-N-*m*-Tolyl-*m*-Nitrobenzohydroxamic Acid.

with aqueous solution of thorium(IV) to form the complex of type, II.



I II

The thermogram recorded for thorium complex in flowing air shows no change in weight initially up

The major products of the chelate decomposition are found by UV, IR and X-ray to the thorium benzoate, benzanilide and finally metal oxide and tars. At about 220°–300° (First exotherm) the vaporisation of benzanilide with a gradual weight loss and about 300°–400° the decomposition of metal benzoate and formation of thorium oxide are expected (second exotherm). Thus the chemical and thermal analyses suggest that N-*m*-T-NBHA forms anhydrous stoichiometric precipitate with thorium and suitable as an analytical reagent for gravimetric estimation.

Thorium is precipitated quantitatively from a solution containing 5–15 mg. of thorium nitrate at

pH 4–4·5 with N-m-T-NBHA. The yellowish precipitate is weighed directly after drying at 110°–120°. The complex is fairly soluble in ethanol and chloroform but only sparingly soluble in ether, benzene, carbon tetrachloride acetone and glacial acetic acid. It is decomposed when treated with concentrated sulphuric, nitric, hydrochloric and perchloric acids. The analytical result indicate the composition of complex as $[C_{14}H_{11}N_2O_4]_4Th$.

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Studies on Copper (II) Tartrate Complexes—Part-II. Copper (II) Complexes with Tartrate, Ammonia and Substituted ammonia

S. C. SAHOO, S. MISHRA, D. C. DAS and S. PANI

Post-Graduate Department of Chemistry, Sambalpur University, Jyoti Bihar, Burla-768017, Sambalpur, Orissa

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Two series of copper(II) complexes of the types, R Cu(OH) T and M Cu(OH) TL (where R = substituted ammonium ions, T = tartrate ion, M = sodium, potassium and ammonium ions, and L = ammonia and substituted ammonia) have been studied. The formation of the ion, Cu(OH)TL_2^- in solution was established by *p*H titration. The equilibrium constants of the reactions :

$Cu(OH)T(H_2O^-)_2 + L \rightleftharpoons Cu(OH)TL(H_2O^-) + H_2O$ and $Cu(OH)TL(H_2O)^- + L \rightleftharpoons Cu(OH)TL_2^- + H_2O$ have been determined. The potential features of bonding in the complexes have been discussed from i.r. spectra.

THE sparingly soluble copper(II) tartrate, Cu-($C_4H_4O_6$) and the soluble complex salts of the type, M Cu(OH) T (where M = sodium, potassium, and ammonium) have been reported by us earlier[1]. Aliphatic amines are weak bases in aqueous solution and can form complex salts of the type, R Cu(OH) T (where R = methyl ammonium, ethyl ammonium etc.). When the aqueous solution of the salts M Cu(OH) T are treated with excess quantity of the corresponding amine (L) another series of complex salts of the type M Cu(OH) TL are formed. The introduction of more amine molecules into the inner sphere of copper(II) ion under higher concentration of amine has been established by *p*H titration in the present study. When an aqueous solution of Na Cu(OH)T.$2H_2O$ is treated with ammonia (or amines) the water molecules are replaced by stepwise reactions.

$$Cu(OH)T(H_2O)_2^- + L \rightleftharpoons Cu(OH)TL.H_2O^- + H_2O \quad \cdots (1)$$

$$Cu(OH)TL(H_2O)^- + L \rightleftharpoons Cu(OH)TL_2^- + H_2O \quad \cdots (2)$$

The i.r. spectra of the complexes have been studied with a view to explore the potential features of bonding in the complexes.

Materials and Methods

All the chemicals used were of AnalaR (B.D.H.) quality. The starting materials, copper(II) tartrate, M Cu(OH)T were prepared by the method reported earlier[1].

I. *Complex salts of the type, R Cu(OH)T*

(R = methyl, ethyl, diethyl and trimethyl ammonium ions).

Copper(II) tartrate went into solution when it was gently heated with a small quantity of aqueous solution of appropriate amine. It was filtered and the filtrate was evaporated to dryness over a water bath. The blue crystalline compound obtained was analysed for copper and tartrate content.

II. *Complex salts of the type M Cu(OH)TL*

(M = sodium, potassium, ammonium and substituted ammonium, L = ammonia and substituted ammonia).

An aqueous solution of the complex salt prepared in method I or M Cu(OH)T was treated with the aqueous solution of the appropriate ligand and evaporated to dryness over a water bath. The solid compound thus obtained was again dissolved in small quantity of water and treated with same ligand and evaporated. The compound obtained after repeating the process three to four times was next analysed.

The copper content of the complexes was estimated as copper sulphide and also iodometrically after the complete removal of ammonia or amine. The filtrate obtained after the removal of copper as sulphide was evaporated to dryness over water bath to remove hydrogen sulphide and free hydrochloric acid. The tartaric acid in the residue was estimated by dissolving the residue in water and titrating against standard alkali. The analytical data of the complexes are recorded in Table 1.

The conductances of the complexes have been measured for dilute solution (0·001*M*) by employing Phillips conductivity bridge with a dip type cell. The molecular conductivity data are recorded in Table 1. The i.r. spectra of some of the complexes have been taken in potassium bromide phase. The molar conductance values indicate the compounds to be 1 : 1 electrolytes.

Experimental

pH titration

(I) To 25 ml of solution containing $1{\cdot}002 \times 10^{-3}$ g.mole of sodium perchlorate, increasing amounts of

TABLE 1

Compound	% calculated		% found		Molecular conductance (Λ_m)ohm^{-1}cm^{2}mole^{-1}
	Cu	T	Cu	T	
1. $CH_3NH_3Cu(OH)T$	24.40	56.82	23·93	55.75	157.4
2. $C_2H_5NH_3$ Cu(OH)T	23.15	53.91	22.67	51.97	140.1
3. $(C_2H_5)_2NH_2Cu(OH)T$	17.00	39.42	18.05	41.78	127.5
4. $(CH_3)_3NH$ Cu(OH)T	22.03	51.31	21.32	50.06	146.0
5. Na Cu(OH)T NH_2CH_3	22.03	52.42	21.40	49.87	180.5
6. Na Cu(OH)T $NH_2C_2H_5$	21.43	49.92	21.96	49.07	153.9
7. $NH_4Cu(OH)T$ NH_3	24.12	56.12	23.92	56.14	153.0
8. K Cu(OH)T NH_2CH_3	21.28	49.57	21.53	50.02	135.5
9. K Cu(OH)T NH_3	22.33	50.01	22.07	49.80	141.3
10. K Cu(OH)T $NH_2(C_2H_5)$	20.33	47.36	20.30	47.33	—
11. K Cu(OH)T $NH(C_2H_5)_2$	18.66	43.47	18.88	43.42	—
12. K Cu(OH)T $N(CH_3)_3$	19.45	45.32	19.19	45.56	143.1
13. K Cu(OH)T $N(C_2H_5)_3$	17.24	40.16	17.19	40.44	154.8
14. $CuT(CH_3NH_2)_2H_2O$	22.43	47.86	21.81	50.71	145.0
15. $CuT(C_2H_5NH_2)H_2O$	19.44	46.32	20.02	47.56	141.6

0·07947*M* ammonium hydroxide solution was added and the *p*H was measured by Cambridge Bench *p*H meter at 26°. The results are graphically represented by curve (A) (Fig. 1) (the *p*H is plotted against mole

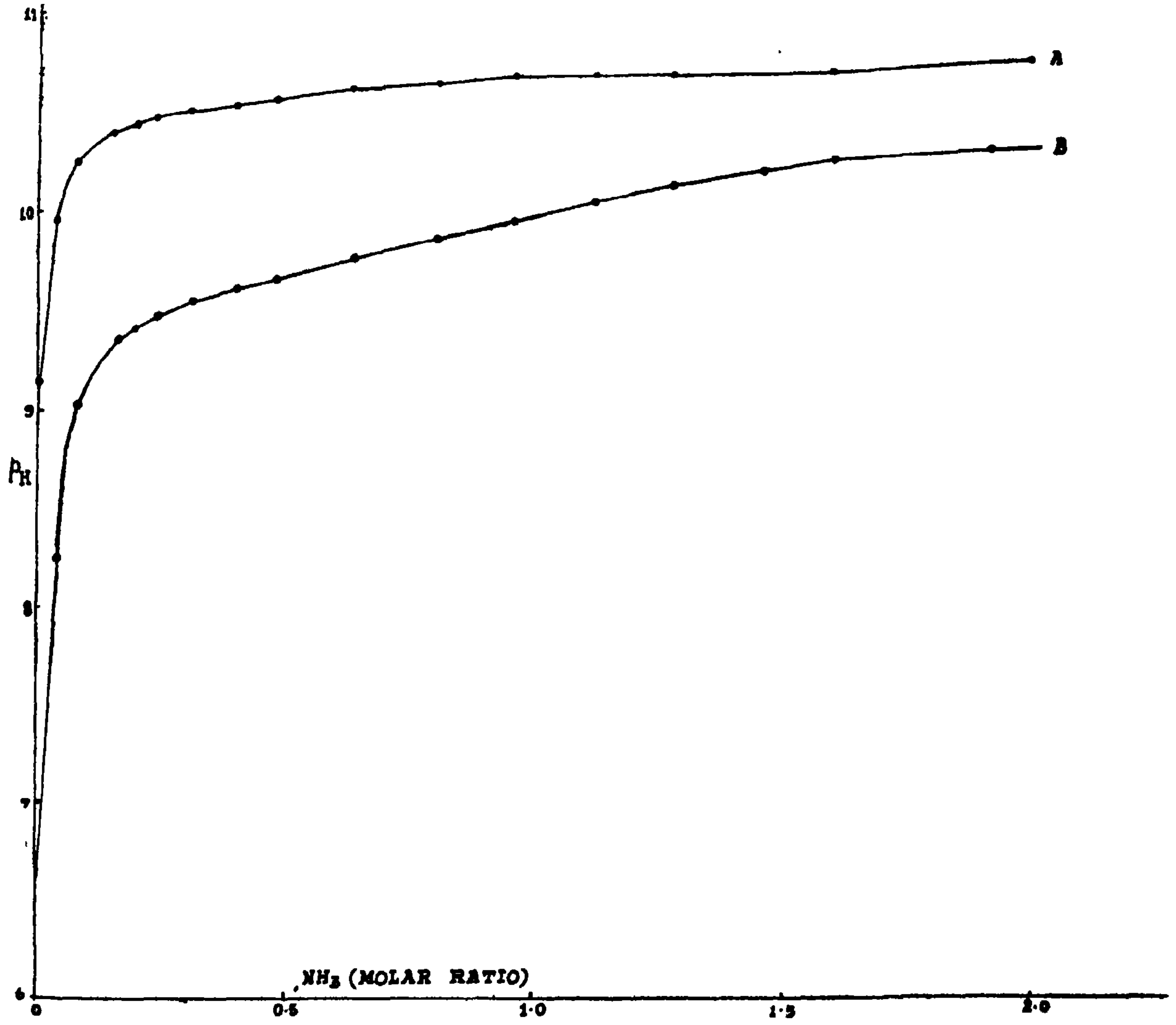


Fig. 1.

ratio i.e., ratio of moles of ligand added to moles of NaCu(OH)T). In another experiment at the same temperature and the same volume of solution containing $1 \cdot 002 \times 10^{-3}$ g.mole of NaCu(OH)T was titrated against the same ammonium hydroxide solution. The results are shown in curve (B) (Fig. 1) Similar experiments were performed with other amines.

(II) In another sets of experiments, 100 ml of solution containing 0·001 g.mole of sodium perchlorate and 0·00945 g.mole of ammonium hydroxide was titrated against 0·6384*M* perchloric acid solution and *p*H was measured. The results are shown in curve (A) (Fig. 2). In a second experiment, 100 ml. of solution containing 0·001 g.mole of NaCu(OH)T and 0·00945 g.mole of ammonium hydroxide was titrated against the same perchloric acid. The results are shown in curve (B) (Fig. 2). Similar experiments were performed using other amines.

Results and Discussion

In experiment (I) the *p*H of the system (B) is lower than that in system (A) for the same volume of ammonium hydroxide added shows that ammonia is removed by $Cu(OH)T^-$ from the solution. At the same *p*H the distance between the two curves gives the amount of ammonia taken by the complex. $\bar{n}$, the average number of ammonia molecule taken by each $Cu(OH)T^-$ ion is obtained by dividing the amlunt of ammonia taken, by the amount of NaCu(OH)T in the solution. $\bar{n}$ varies from 0 to 2. The concentration of free ammonia in system (B) is calculated in the following manner.

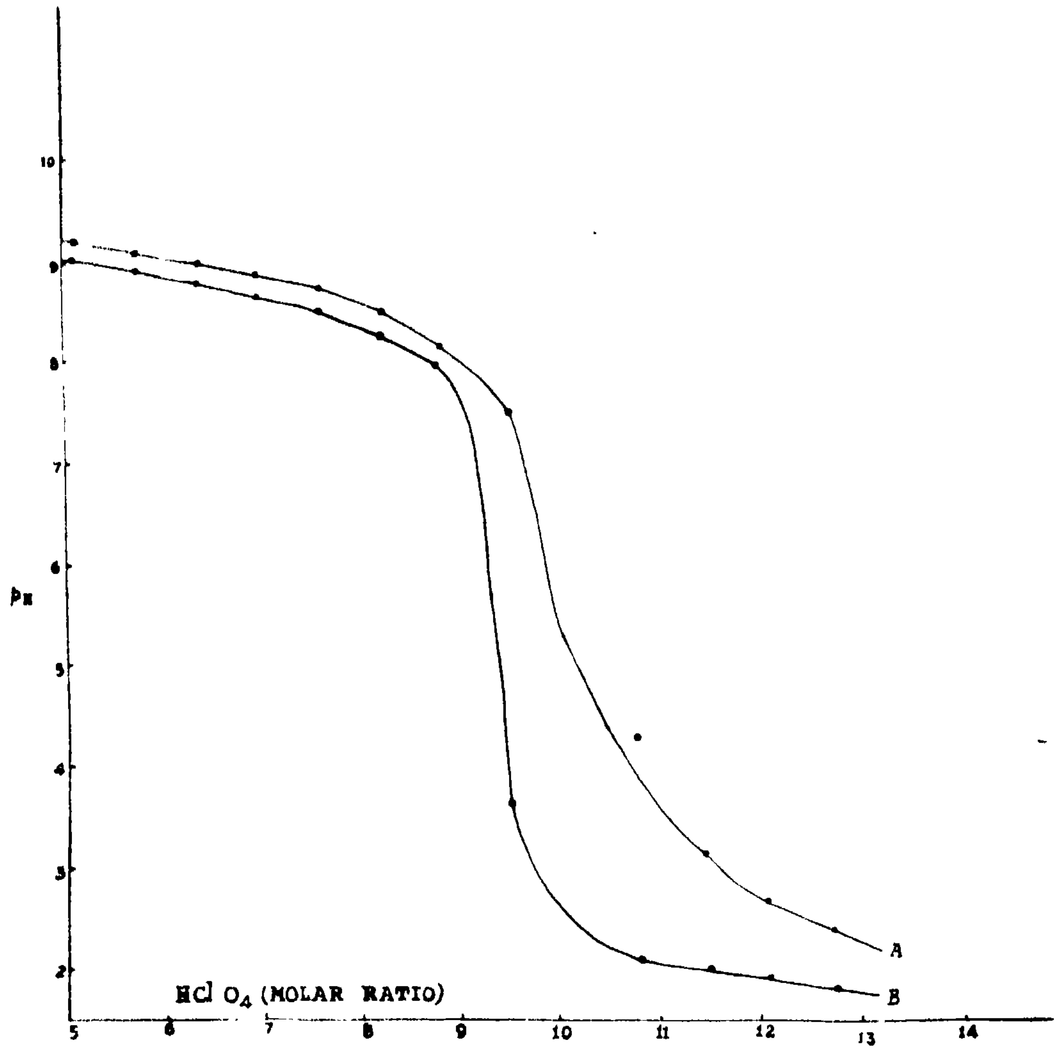


Fig. 2.

The total amount of ammonia added in system (B) $= [NH_3]_T$

The amount of ammonia taken by the complex $= [NH_3]_B$

The amount of ammonium ion in the solution $= [NH_4^+]$

The amount of free ammonia in the solution $= [NH_3]$

$$[NH_3]_T = [NH_3]_B + [NH_4^+] + [NH_3]$$

or

$$[NH_3]_T - [NH_3]_B = [NH_4^+] + [NH_3]$$

or

$$NH_3 = \frac{[NH_3]_T - [NH_3]_B}{1 + K[H^+]} \quad \ldots (3)$$

where, K is the equilibrium constant of the reaction,

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \quad \ldots (4)$$

The value of K is determined from the direct titration of ammonia against perchloric acid in experiment (II) and used for calculation of $[NH_3]$. The equilibrium constants K_1 and K_2 are obtained from the formation curve, $\bar{n}$ is plotted against $\log \frac{1}{[NH_3]}$ and $\log K_1$ and $\log K_2$ are obtained corresponding to $\bar{n} = 0{\cdot}5$, 1 and 1·5 respectively. The values with those of other systems are collected in Table 2.

The ratio of K_1 and K_2 is small in all these cases and hence the values obtained are approximate values which are corrected by Schroder method[2]. The corrected values are also recorded in Table 2.

TABLE 2

Ligand solution	Equilibrium constants from formation curve		Correct equilibrium constants by Schroder method	
	log K_1	log K_2	log K_1	log K_2
NH_3	3.24	2.67	2.52±0.18	3.38±0.18
CH_3NH_2	3.38	2.37	3.23±0.18	2.52±0.18
$C_2H_5NH_2$	3.42	2.36	3.29±0.18	2.49±0.18
$(C_2H_5)_2NH$	3.04	2.39	2.56±0.25	2.87±0.25
$(CH_3)_3N$	3.65	2.77	3.43±0.25	2.99±0.25
$(C_2H_5)_3N$	3.30	2.37	2.85±0.25	2.81±0.25

It is of interest to note that in the ammonia system the corrected value of K_2 is greater, whereas in other case it is less. This means that the six co-ordination complex, $Cu(OH)T, (NH_3)_2^-$ is preferred to the five coordination complex, $Cu(OH)T(NH_3)^-$. In case of other complexes the ligands enter in stepwise reaction probably due to the presence of alkyl groups in the ligand.

In experiment-II, the two curves (A) and (B) very nearly coincide till one third of the ammonia is neutralised by the acid. After that the two curves diverge and the pH of the system (B) is lower than that of the system (A) for the same amount of acid added. This means that the amount of free ammonia in the system (B) is less, due to complex formation. The amount of ammonia bound to the complex can be determined as follows. As a first approximation it is assumed that the acid added reacts completely with ammonia to give ammonium ion in both the systems, consequently the reaction (1) and (2) in the system (B) proceed in the reverse direction. Let A and B be two points on curve (A) and (B) respectively cut by the same pH axis. The concentration of total amount of ammonia at A and B are represented by $[NH_3]_T^A$ and $[NH_3]_T^B$. The concentrations of other constituents at A and B are represented by $[\ ]_A$ and $[\ ]_B$ respectively.

$$[NH_4^+]_A = [HClO_4]_A$$

$$[NH_4^+]_B = [HClO_4]_B$$

$$[NH_3]_T^A = [NH_4^+]_A + [NH_3]_A.$$

Since certain amount of ammonia is bound to the complex at B, the amount of free ammonia at B, $[NH_3]_B$ is obtained as follows. At the same pH

$$\frac{[NH_3]_A}{[NH_4^+]_A} = \frac{[NH_3]_B}{[NH_4^+]_B}. \quad \ldots (5)$$

In the above equation except $[NH_3]_B$ the other quantities are known. Hence $[NH_3]_B$ is calculated by equation (5). The amount of ammonia bound to the complex is given by :

$$[NH_3]\ \text{Bound} = [NH_3]_T^B - ([NH_4^+]_B + [NH_3]_B) \quad \ldots (6)$$

$\bar{n}$ the average number of ammonia bound to each $Cu(OH)T^-$ ion is obtained by dividing $[NH_3]$ bound by $[NaCu(OH)T]$. $\bar{n}$ is plotted against $\log \frac{1}{[NH_3]}$ and $\log K_1$, $\log K_2$ obtained from this curve are respectively 2·37 and 1·57. These values do not agree with those obtained by direct titration method. The lower values obtained due to some other reactions taking place with acid simultaneously.

In the system (A) ammonia is completely neutralised when 14·8 ml of perchloric acid is added and the pH rapidly comes down when the end point is exceeded. In the system (B) also this decreases after addition of 14·8 ml of perchloric acid but the fall of pH is less rapid indicating another reaction to be taking place at lower pH. The probable reaction is,

$$Cu(OH)T^- + H^+ \rightleftharpoons CuT(Sol) \quad \ldots (7)$$

For the calculation of the equilibrium constant of reaction (7) it is assumed that all the ammonia present in the system (B) is completely neutralised when 14·8 ml of perchloric acid is added. Acid excess above this amount reacts with $Cu(OH)T^-$ to

give CuT(Sol). The equilibrium constant of the reaction (7) is calculated as follows. Excess of acid above that required for neutralisation of ammonia $= [HClO_4]_E$. The amount of hydrogen ion taken by $Cu(OH)T^- = [HClO_4]_E - [H^+]$. The amount of hydrogen ion in the solution is calculated from the *p*H. The average number of protons taken by $Cu(OH)T^-$ is given by :

$$\frac{[HClO_4]_E - [H^+]}{[NaCu(OH)T]} = \bar{n}$$

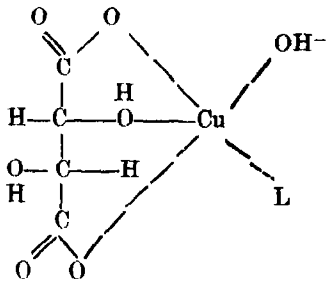
$\bar{n}$ is plotted against *p*H and at $\bar{n} = 0{\cdot}5$ log *k* is found to be 6·25. Patel, Satpathy and Pani have reported *p*K of the reverse reaction to be 5·59. This difference might be due to the existence of $Cu(OH)T(NH_3)^-$ after the addition of required amount of acid to neutralise ammonia.

The i.r. spectra of a few complexes are recorded in table 3

TABLE 3

Compound	Absorption bands in cm^{-1}			
$NH_4Cu(OH)T.NH_3$	1600	1375	1110 and 1055	430
$CH_3NH_3Cu(OH)T.NH_2CH_3$	1610	1365	1105 and 1060	440
$NaCu(OH)T.NH_2CH_3$	1605	1365	1105 and 1055	444
CH_3 NH Cu(OH)T.	1605	1370	1105 and 1055	

Krischner and Keisling have reported[3] sharp absorption bands at 1750 and 1097 cm^{-1} in the infrared spectra of *d*-tartaric acid. The former has been assigned to the carboxylic acid groups and the latter to the C–O stretching of the secondary alcoholic groups. In sodium potassium tartrate a strong band and a medium band are observed at 1615 cm^{-1} and 1460 cm^{-1} respectively. These are due to symmetric and antisymmetric vibration of the carboxylate groups. In these compounds a strong and sharp band is observed at 1610 to 1600 cm^{-1} but no band is observed at about 1460 cm^{-1}. This indicates that both the carboxylate groups are coordinated. Goulden has reported[4] that in lactate tion the secondary alcoholic groups has an inplane O–H bonding absorption band at 1275 cm^{-1} which is shifted to 1390 cm^{-1} upon chelation of secondary alcoholic group. The band at 1365 to 1375 cm^{-1} in these compounds might be due to chelation of alcoholic group. Instead of a single band at about 1097 cm^{-1} as reported for -*d*-tartaric acid a split band at 1110 and 1055 cm^{-1} is observed in all the complexes, which indicates that the two secondary alcoholic groups are different. This means that one of the two alcoholic groups is coordinated. The absorption band observed at about 500 cm^{-1} in cobalt(III) amines has been assigned to Co(III)-N stretching frequency by Powell and Sheppard[5] and also Nakamoto[6]. Shimanouchi and Nakagawa[7] made a normal coordinate analysis of the $Co(NH_3)_6^{3+}$ ion and assigned to the Co-N stretching mode a weak band at 464 cm^{-1}. In the present study weak bands are found in the region 430–444 cm^{-1} in a few cases. These absorption bands are most probably due to Cu-N stretching mode. The structure of $Cu(OH)TL^-$ ion can be represented by :



There might be a coordinated water molecule in the complex and is replaced by another ligand in $Cu(OH)TL_2^-$.

Acknowledgement

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N-α-Pyridyl-N′-Benzoyl Thiourea as a Chelating Agent for the Determination of Rhodium

D. K. DAS*, M. MAZUMDAR and S. C. SHOME

Chemical Laboratories, Presidency College, Calcutta-700 012

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N-α-pyridyl-N′-benzoyl thiourea is a useful chelating agent for the gravimetric as well as spectrophotometric determination of rhodium(III). The metal chelate is precipitated in the pH range of 3.5 to 5.5 and can be weighed as $Rh(C_{13}H_{10}N_3OS)_3$. Rhodium(III) is determined gravimetrically with the thio-ligand in presence of palladium(II), platinum(IV), iridium(IV), osmium (VI), ruthenium(III) and commonly associated base metals by the use of masking agents or controlling the acidity of the solution.

The light brown chelate formed by rhodium with N-α-pyridyl-N′-benzoyl thiourea can be extracted quantitatively with chloroform in the pH range 5.24–6.3 in presence of ethanol. The extract obeys Beer's law at 360 nm over the concentration ranging from 0.69 μg Rh ml^{-1} to 6.9 μg Rh ml^{-1}. The colour of the extract is stable for 24 hours. It is possible to determine microgram quantities of rhodium(III) spectrophotometrically using N-α-pyridyl-N′-benzoyl thiourea as a colour forming reagent in presence of most of base metals and all other platinum metals. The sensitivity of the colour reaction and the molar absorptivity of the complex are 0.0102 μg Rh cm^{-2} and 9.54×10^3 $l.mole^{-1}$ cm^{-1} respectively. Cyanide ion, however, interferes with the spectrophotometry of the metal.

NONE of the organic thio compounds which were employed by earlier investigators[1-7], can be recommended for either gravimetric or spectrophotometric determination of rhodium. N-α-pyridyl-N′-benzoyl thiourea (PBT) was used by Shome and co-workers[8] as a chelating agent for the determination of osmium(VI). In the present work PBT is employed for the gravimetry and spectrophotometry of rhodium(III). Rhodium(III) forms a light-brown complex with the thio-ligand which can be weighed as $Rh(C_{13}H_{10}N_3OS)_3$. The metal can be precipitated with PBT in presence of commonly associated base metals using suitable masking agents. It is separated from other platinum metals by either adjusting the acidity of the solution or prior reduction of the interfering ions. Iridium(IV), however, does not affect this determination. The rhodium chelate is soluble in common organic solvents and can be extracted with a mixture of ethanol and chloroform to produce a yellowish brown solution. The extract obeys Beer's law at 360 nm. The colour of the extract is stable for more than 24 hrs. Rhodium is separated from various foreign ions by extraction and subsequently determined spectrophotometrically.

Experimental

Apparatus : A Carl-Zeiss spectrophotometer, PMQ-II model with 1 cm quartz cells, was used for the absorbance measurements. A Cambridge *p*H meter (Bench model) was employed for all *p*H measurements, standardised at *p*H 4·0 and at *p*H 9·27.

* Present Address: Chemical Laboratories, Central Ground Water Board, Eastern Region, 24, Park Street, Calcutta 700016, India.

Reagents and Chemicals

Standard rhodium(III) solution : The standard solution was prepared by dissolving rhodium(III) chloride in dilute hydrochloric acid. The metal content of the solution was determined by precipitating the metal with formic acid. The precipitate was ignited to pure metal by heating in a current of hydrogen. For spectrophotometric determination, weaker solutions were prepared by proper dilution of the stock solution.

Diverse ion solutions : Solutions of diverse ions were prepared by dissolving known amounts of pure compounds in distilled water. Dilute hydrochloric acid was used where required.

Reagent solutions : 1% solution of PBT in 50% acetic acid solution was used for precipitation of rhodium(III). For spectrophotometric measurements, 0·01*M* reagent in ethanol was used.

All the reagents used were of A.R. grade.

Gravimetric determination of rhodium

Procedure : Dilute a known amount of rhodium(III) solution to about 200 ml with distilled water in a beaker. Warm the solution to about 60°–70° and add slowly 3–4 times the theoretical amount of 1% PBT solution in 50% acetic acid with constant stirring. Adjust the *p*H of the solution to 3·5-5·5 by adding dropwise 4(*N*) ammonia solution with constant stirring. Place the beaker on a boiling water bath and digest the light yellow precipitate formed for 1–2 hr with occasional stirring. Filter the precipitate on a no. 4 sintered glass crucible. Wash the precipitate with 1% hot acetic acid solution. Dry

the complex at 110°–120° in an oven for 2 hrs, cool in a desiccator and weigh as $Rh(C_{12}H_{10}N_3OS)_3$. Calculate the metal content on the basis that the precipitate contained 11·82% of rhodium. The results are given in Table 1.

TABLE 1 – GRAVIMETRIC DETERMINATION OF RHODIUM

Rh-taken (mg)	Foreign ion added (mg)	Rh-found (mg)	Error (mg)
3.75	–	3.78	+0.03
7.14	–	7.12	–0.02
11.25	–	11.26	+0.02
7.51	$^{a}Cu^{2+}$ (150)	7.52	+0.01
7.51	$^{b}Fe^{3+}$ (150)	7.53	+0.02
7.51	$^{a}Ni^{2+}$ (200)	7.51	0.00
7.51	$^{a}Hg^{2+}$ (250)	7.52	+0.01
7.51	$^{a}Ti^{4+}$ (250)	7.51	0.00
7.51	$^{a}Cr^{3+}$ (200)	7.52	+0.01
7.51	$^{c}Mn^{2+}$ (200)	7.50	–0.01
7.51	$^{c}Tl^{3+}$ (200)	7.51	0.00
7.51	$^{a}Al^{3+}$ (150)	7.51	0.00
7.51	$^{c}Mo^{6+}$ (150)	7.53	+0.02
7.51	$^{a}W^{6+}$ (200)	7.51	0.00
7.51	$^{c}UO_2^{2+}$ (300)	7.52	+0.01
7.51	$^{c}Th^{4+}$ (300)	7.49	–0.02
7.51	$^{a}V^{5+}$ (150)	7.51	0.00
7.51	$^{a}Cd^{2+}$ (300)	7.50	–0.01
7.51	$^{c}Au^{3+}$ (300)	7.52	+0.01
7.51	Pd^{2+} (100)	7.51	0.00
7.51	Pt^{4+} (90)	7.52	+0.01
7.51	Ir^{4+} (150)	7.53	+0.02
7.51	$^{d}Os^{6+}$ (250)	7.51	0.00
7.51	$^{e}Ru^{3+}$ (250)	7.51	0.00

a = In presence of EDTA, *b* = In presence of fluoride; *c* = In presence of tartrate, *d* = In presence of sulphur dioxide, *e* = In presence of hydroxylamine hydrochloride.

The complete precipitation of the chelate took place in the *p*H range 3·5 to 5·5 when the supernatant liquid contained about 0·01% (w/v) of the reagent in excess, keeping the other conditions same.

Rhodium was determined with PBT in a mixture containing known amounts of diverse ions and the results are shown in Table 1. The metal was separated from the base metals using EDTA, tartrate or fluoride ions as masking agents. Rhodium was separated from palladium or platinum by precipitation of the latter with PBT in 0·5*N* hydrochloric acid medium. The metal was also precipitated with the reagent in presence of osmium(VI) and ruthenium(III) by prior reduction of the latter metal ions with sulphur dioxide and hydroxylamine hydrochloride respectively.

The rhodium complex is stable in dilute hydrochloric acid or sulphuric acid but decomposes in nitric acid. The chelate is soluble in chloroform, ethanol and partly soluble in benzene. The results of analysis of the pure complex, dried at 120°, are as follows: Found: Rh = 11·80%; N = 14·40%; S = 11·00%. Required for $Rh(C_{12}H_{10}N_3OS)_3$: Rh = 11·82%; N = 14·46%; S = 11·02%.

Spectrophotometric determination of rhodium(III)

Procedure: In a 100 ml separatory funnel, introduce a measured amount of rhodium(III) solution and adjust the *p*H of the solution 5·24–6·3 by the addition of dilute hydrochloric acid and 10% sodium acetate solution. Mix the solution with an excess amount of 0·01*M* ethanolic solution of PBT by shaking vigorously and place the funnel with its contents over a boiling water bath for about 25–30 mins. Cool the separatory funnel to room temperature and shake the precipitate 2–3 times with 5 ml portions of chloroform followed by the addition of 5 ml of ethanol. Separate and dilute the yellowish brown complex extract into a 25 ml volumetric flask with chloroform. Dry over anhydrous sodium sulphate and measure the absorbance against reagent blank prepared under the same conditions with the same quantity of the reagent.

Results and Discussion

Absorbance curves of the extracts containing varying concentrations of rhodium ranging from 1·38 $\mu g\ ml^{-1}$ to 5·52 $\mu g\ ml^{-1}$ at *p*H 5·5 are shown in Fig. 1. The spectral absorbance of the complex was studied over the wavelengths ranging from 310 nm to 410 nm. The curves showed maximum absorption at 340 nm. The extract of the complex obeyed Beer's law at 360 nm over the concentration range 0·69 μg Rh ml^{-1} to 6·9 μg Rh ml^{-1}. Since the reagent has slight absorption at 340 nm, all the spectral measurements were made at 360 nm. The most suitable *p*H range for complete extraction of the rhodium chelate from aqueous phase was found to be 5·24 to 6·30 when the reagent concentration was ten times to that of rhodium(III) ion concentration.

The sensitivity of colour reaction and molar absorptivity of the rhodium chelate were calculated and found to be 0·0102 μg Rh cm^{-2} and $9{\cdot}54\times10^{3}$ $l.mole^{-1}cm^{-1}$ at 360 nm respectively. The relative mean error and the coefficient of variation of the procedure were found to be 0·23% and 0·64% respectively.

Nature of the complex: The empirical formula of the rhodium(III)-PBT complex in ethanol-chloroform mixture was assigned by mole-ratio method as described by Meyer and Ayres[9]. The results, shown in Fig 2 clearly indicate that the stable complex was formed between the rhodium and N-α-pyridyl-N′-benzoyl thiourea in the ratio 1 : 3. The composition of Rh(III)-PBT complex was verified by conventional slope-ratio method.

The dissociation constant[10] of the rhodium complex was determined from the mole-ratio curve and found to be $2{\cdot}8\times10^{-15}$.

Effect of diverse ions: Rhodium(III) was separated and determined with PBT in presence of diverse ions

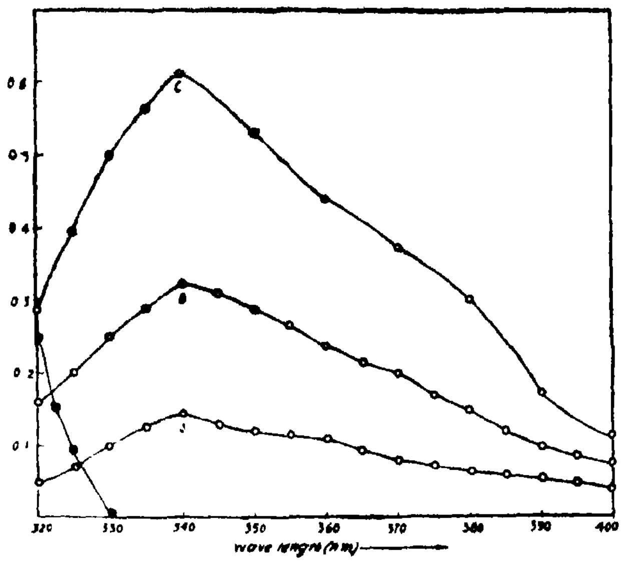


Fig. 1. Absorbance curves of Rhodium(III) N-α-Pyridyl-N[1] benzoyl thiourea, complex in ethanol-chloroform mixture A = 1.38 μg Rh ml^{-1}, B = 2.76 μg Rh ml^{-1}, C = 5.52 μg Rh ml^{-1} ◐ = 10—4 *M* veagent

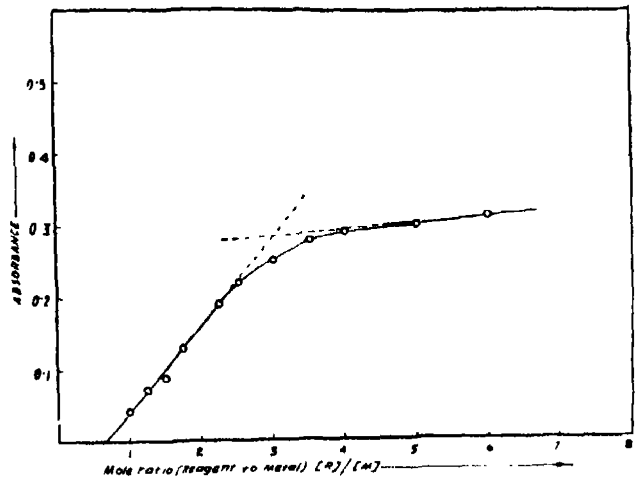


Fig 2. Composition study by mole-ratio method applied to Rhodium(III) N-α-Pyridyl-N'- benzoyl thiourea complex in ethanol Chloroform mixture.

as described under the procedure. In the study of the effect of diverse ions, tartrate was added to prevent the hydrolysis or complex formation of some foreign ions. Interferences of copper, nickel, iron and mercury were avoided by masking with EDTA and of titanium with fluoride ions. Palladium(II) was removed by extraction with PBT in chloroform at room temperature in 0·1(*N*) hydrochloric acid. Rhodium was separated from platinum by the prior extraction of the latter with PBT in 0·5 (*N*) hydrochloric acid solution and the metal was determined in the aqueous layer after raising its *p*H to 5·5. Iridium(IV), osmium(IV) and ruthenium(II) did not interfere with the extraction and subsequent spectrophotometric determination of the metal with the chelating ligand. Cyanide ions, however, interfered. The tolerance limit for the foreign ions was taken as the largest amount which deviated the absorbance due to rhodium(III) by not more than 2 per cent. The results are given in Table 2.

TABLE 2—EFFECT OF DIVERSE IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF RHODIUM(III)

Rhodium taken = 57.6 μg

Foreign ion added	Amount tolerated (μg)	Foreign ion added	Amount tolerated (μg)
$^{a}Fe^{3+}$	2000	$^{b}W^{6+}$	2000
$^{a}Cu^{2+}$	2000	$^{b}V^{5+}$	1500
$^{a}Ni^{2+}$	2500	$^{b}UO_2^{2+}$	2000
$^{a}Hg^{2+}$	2000	$^{b}Tl^{3+}$	2000
$^{b}Al^{3+}$	2500	$^{b}Pb^{2+}$	2000
$^{b}Co^{2+}$	2500	Au^{3+}	2000
$^{c}Ti^{4+}$	2500	Pt^{4+}	2000
$^{b}Cd^{2+}$	3000	Pd^{2+}	3000
$^{b}Mn^{2+}$	3000	$^{d}Os^{8+}$	2000
$^{b}Zn^{2+}$	3000	$^{e}Ru^{3+}$	2000
$^{b}Mo^{6+}$	1500	Ir^{4+}	1000

a = In presence of EDTA, *b* = In presence of tartrate, *c* = In presence of fluoride, *d* = In presence of sulphur dioxide, *e* = In presence of hydroxylamine hydrochloride.

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Nature of Metal Chloride Complexes in Organic Solvent Media. Part I—Iron(III)

G. S. MURTY and M. N. SASTRI*

Department of Chemistry, Andhra University, Waltair

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The nature of Fe(III) species that exist in different organic solvent systems like ethanol, DMSO and acetone are investigated. Ion-exchange, conductivity and spectral studies indicate the Fe(III) species as anionic $FeCl_4^-$ in ethanol, cationic $FeCl^{++}$ in DMSO and polymeric $(FeCl_3)_x$ in acetone.

THE anion exchange uptake of Fe(III) from organic solvent media containing hydrochloric acid has been investigated by several workers[1-4]. Studies in this laboratory showed that the anion exchange uptake of Fe(III) increased with addition of methanol and ethanol, but there was a sharp decrease with acetone and with DMSO (dimethyl sulfoxide). From this it appears that the nature of the Fe(III) species differs with the solvent medium. This is further confirmed by conductometric, spectrophotometric and far I.R. studies. We describe some of our studies in this communication.

Experimental

Ion-exchange Resin : Amberlite IRA-400 "Analytical grade" anion exchange resin (−70 +100 mesh) of Rohm and Haas was used in the chloride form.

Metal solution : A 0·05M stock solution of ferric chloride was prepared from E.Merck sample of $FeCl_3.6H_2O$ and standardised against standard EDTA solution[5].

Tetramethyl Ammonium Tetrachloroferrate (III) (TMATCF) : The complex TMATCF was prepared according to the procedure of Cotton and Goodgame[6].

Organic solvents : All the solvents were purified by standard methods.

Radioactive tracer : γ-active iron (^{59}Fe $t_{\frac{1}{2}} = 45$ days) was obtained from Bhabha Atomic Research Centre as $FeCl_3$ in HCl solution with a specific activity of 4 Ci per g.

Equipment

Conductivity measurements : A Philips model PR 9500/90 direct measuring conductivity bridge with a magic eye indicator giving an accuracy of ±2·5% was used. The measurements were carried out at 28·0±0·1°.

Spectrophotometric measurements : Visible and ultraviolet spectra were taken on a UVSPEK spectrophotometer using 1 cm matched silica cells. I.R. Spectra were obtained on a Beckman-12 I.R. Spectrophotometer.

Radioactivity measurements : The ^{59}Fe γ-activity was estimated with a NaI(Tl) scintillation crystal coupled to a single channel γ-ray spectrometer (ECIL Model GRS 20 B).

Distribution coefficient values K_d : Distribution coefficients for Fe(III) were determined by batch equilibration method using the equation[7]

$$K_d = \frac{\text{Volume of the solution in ml}}{\text{Weight of the resin in g.}} \times \frac{\text{Activity on the resin}}{\text{Activity in the solution}}.$$

Results

Ion-exchange studies : The K_d values for Fe(III) as a function of organic solvent concentration in different organic solvents (methanol, ethanol, acetone and DMSO)-hydrochloric acid—water systems are given in figure 1 from which it is seen that while the anion exchange uptake of Fe(III) from hydrochloric acid solution containing methanol or ethanol is high, the uptake is negligible in acetone and DMSO. It is also observed that when acetone or DMSO is added to the alcohol-HCl system the high K_d values obtaining in the alcohol-HCl systems showed a marked decrease in uptake (Fig. 2).

Conductance studies : The molar conductance (Λ_M) values of the TMATCF complex in various solvents at 0·001M concentration (Table 1) show that it behaves as 1 : 1 electrolyte in the solvents ethanol and acetone. On the other hand in DMSO the value is nearer to a 1 : 2 electrolyte value.

Spectrophotometric studies: The spectra of the complex TMATCF in ethanol and DMSO in 200–400 nm region are given in Fig. 3. The spectral characteristics of $FeCl_4^-$ in aqueous and non-aqueous media have been reported by several workers[8–14]. Uri and Brealy[14] assigned the peak at 310 nm as characteristic of $FeCl_4^-$ since this peak is fully pronounced with added excess of LiCl whereas the peaks at 244 nm and 365 nm are present even prior to the

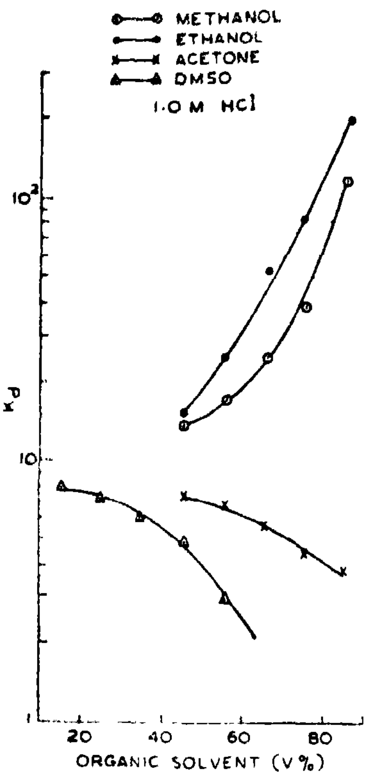


Fig. 1. Anion exchange uptake of Fe(III) from solvent systems.

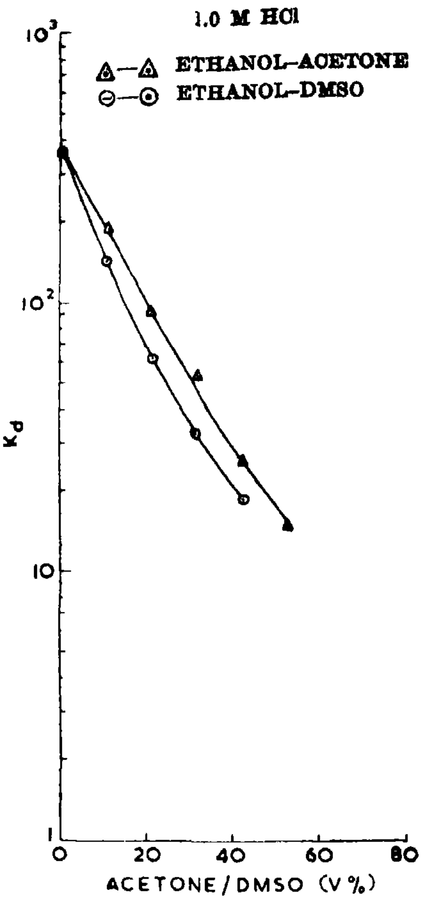


Fig. 2. Anion exchange uptake of Fe(III) from mixed solvent systems.

Table 1

Molar conductance values of the TMATCF complex (ohms^{-1} cm^2 mole^{-1})

Solvents	Experimental	Expected Ranges* 1 : 1 Electrolyte	Expected Ranges* 1 : 2 Electrolyte
Ethanol	47	35—45	70—90
Methanol	105	80—115	160—220
Acetone	116	100—140	160—200
DMSO	68	37—43	70—80**

* W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81.

** M. N. Sastri and G. S. Murty, (unpublished results).

Note: The Λ_M values for 1 : 3 electrolytes in DMSO are about 110 (S. K. Ramalingam and S. Soundararajan, *J. Inorg. Nuclear Chem.*, 1967, 29, 1763). Hence the values obtained by us for 1 : 2 electrolytes in this solvent appears reasonable.

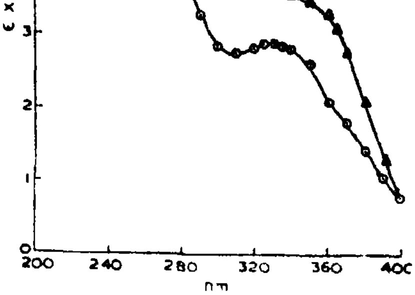


Fig. 3. Absorption spectra of the complex TMATCF (with added chloride).

addition of LiCl. Since our results also conform to those, we proceed on the assumption that the 310 nm peak characterises the $FeCl_4^-$ species. The spectrum in ethanol indicates the existence of $FeCl_4^-$. On the other hand there is no evidence for the formation of $FeCl_4^-$ in DMSO even when a large concentration of chloride ion was present. In this solvent a single peak is observed at 335 nm. In acetone it has not been possible to identify the peaks in UV region because of strong absorption of the solvent in this region. But the peak at 365 nm showed a significant increase in ϵ with dilution (Table 2).

TABLE 2—MOLAR EXTENTION COEFFICIENT VALUES (ϵ) OF Fe(III) IN ACETONE (λ_{max} = 365 nm)

Fe(III) concentration	ϵ
1.00×10^{-4}	5.10×10^3
8.17×10^{-5}	6.42×10^3
4.08×10^{-5}	7.34×10^3

Such marked alterations in values can be taken as an indication for the existence of polymeric species[16].

Discussion

The aim of this study is to seek an explanation for the anamolous anion exchange behaviour of Fe(III) in the non-aqueous solvent systems DMSO and acetone. The conductivity value for the TMATCF complex in DMSO shows that the complex does not exist as 1 : 1 electrolyte but undergoes a change through solute-solvent interaction. The spectrophotometric studies of Drago *et al*[17] and also our present studies show that $FeCl_4^-$ does not exist in DMSO even in the presence of excess Cl^- concentration. This is also confirmed by our far infrared (200–400 cm^{-1}) spectral studies of the complex as mull in DMSO, in which the peak characteristic of $FeCl_4^-$ at 385 cm^{-1} disappeared completely indicating a strong solute-solvent interaction. The spectrophotometric characterisation of Fe(III) species in acetone is not possible because of the fact that the region below 350 nm is strongly absorbed by the solvent. The far infrared spectrum of the complex in MIBK, a less volatile ketone, also shows significant changes indicating a marked solute-solvent interaction.

Lederer[18] subjected Fe(III) in strong HCl to electrophoresis and observed that Fe(III) is present as anionic $FeCl_4^-$. Subrahmanyam[2] carried out similar studies with Fe(III) in 85% ethanol—1·0*M* HCl and established the existence of Fe(III) as anionic $FeCl_4^-$. But when ethanol is replaced by acetone he observed no movement of the Fe(III) spot indicating that under the conditions Fe(III) exists as uncharged species. Although the conductivity data in acetone indicate a 1 : 1 electrolyte, it cannot be taken as evidence for the existence of $FeCl_4^-$ since the spectrophotometric evidence at 365 nm peak favours the formation of a polymeric Fe(III) species. A significant observation in our present studies was that the complex TMATCF could be prepared using only ethanol as solvent and the yields were almost quantitative. On the other hand, all attempts at preparing this complex using acetone and DMSO as solvents have failed. Further, the pure complex showed high solubilities in these solvents. From these observations we conclude that Fe(III) exists as the anionic $FeCl_4^-$ only in ethanol medium, while in acetone and DMSO the existence of different species has to be assumed.

The general coordination model as applicable to many acids dissolved in nonaqueous polar solvents has been discussed by Meek[19] and Gutman[20]. The case of $FeCl_3$ is taken as an example by Meek according to whom several important features of the solvents determine the position of the equlibrium resulting a stepwise replacement of Cl^- ions by solvent molecules. The position of the equilibrium depends upon the ability of each solvent to be associated with the metal ion and to displace the Cl^- ions as schemed below :

$$\underset{\text{(Solid)}}{(FeCl_3)_n} + S \rightarrow [(FeCl_3)_x S_y] \underset{(-S)}{\overset{(+S)}{\rightleftharpoons}} (FeS_4Cl_2)^+ + FeCl_4^-$$

$$FeCl_4^- + S \rightleftharpoons FeCl_3.S + Cl^-$$

$$2(FeCl_3.S) + 2S \rightleftharpoons (FeS_4Cl_2)^+ + FeCl_4^-$$

$$S + (FeS_4Cl_2)^+ \underset{(-S)}{\overset{(+S)}{\rightleftharpoons}} (FeS_5Cl)^{2+} + Cl^- \underset{(-S)}{\overset{(+S)}{\rightleftharpoons}} (FeS_6)^{3+} + Cl^-$$

It is generally observed that

(1) the solvents which coordinate strongly with metal ions will replace the halide ligands from the first coordination sphere more extensively than poorly coordinating solvents.

(2) the more polar strongly coordinating solvents will tend to shift the equilibria towards more complete solvation.

So, from the foregoing discussion it appears that in the case of DMSO, the predominant species of Fe(III) is $[Fe(DMSO)_5Cl]^{2+}$ as already established by Drago *et al.*[17] which can account for the non uptake by the anion exchange resin. The predominant species of Fe(III) in acetone may be represented as $(FeCl_3)_x.S_y$ which cannot be expected to be taken up by the ion exchanger. The conductivity value corresponding to 1 : 1 electrolyte observed for the complex in acetone can be explained to arise from the following solute-solvent interaction step, leading to the formation of a 1 : 1 electrolyte of a different nature.

$$x[(CH_3)_4N\ FeCl_4] + yS(\text{solvent}) \rightleftharpoons (FeCl_3)_x.S_y + x(CH_3)_4N^+ + xCl^-.$$

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1-(2-Quinolylazo)-2-acenaphthylenol (QAAc) as a Selective and Sensitive Chromogenic Reagent for Microdetermination of Palladium (II)

ISHWAR SINGH, B. S. GARG and R. P. SINGH

Department of Chemistry, University of Delhi, Delhi-110007

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Palladium forms two coloured complexes, viz., green and red, with 1-(2-quinolylazo)-2-acenaphthylenol, at low and high pH's respectively. The green (1:1) complex has an absorbance maximum at 670 nm with the sensitivty of 0.0075 μg cm^2. The red (1:2) complex exhibits maximum absorbance at 550 nm and the sensitivity of the colour reaction is 0.0049 $\mu g/cm^2$. The reagent has been employed for microdetermination of palladium in synthetic solutions containing other metals present in alloys.

VARIOUS chromogenic reagents used for microdetermination of palladium have been reviewed by various workers[1,2]. Among the various heterocyclic azo dyes; PAN[3], PAR[3] and TAR[4] have been satisfactorily used for spectrophotometric determination of palladium(II). In the present communication, the sensitive reaction of another heterocyclic azo dye, 1-(2-quinolylazo)-2-acenaphthylenol (QAAc), with palladium has been explored extensively for the micro determination of palladium, both at low and high *p*H levels, in presence of various foreign ions. The method has been found to be fairly selective.

Experimental

Reagents. Stock solution pf palladium(II) was prepared by dissolving appropriate amount of palladium chloride (Johnson and Matthey, London), in $2N$ hydrochloric acid. The solution was standardised gravimetrically with dimethylglyoxime.

QAAc was synthesised[5] and its stock solution was obtained by dissolving the requisite quantity in pure methanol. In no case reagent solutions older than a week were used.

Sodium acetate, hydrochloric acid and sodium hydroxide (reagent quality) were used for *p*H adjustments. Acetate or KCl/HCl buffers were employed.

Apparatus : A Unicam spectrophotometer, SP-600, with 10 mm matched glass cell was used for absorbance measurements.

A Metrohm *p*H meter, type E-350, with saturated calomel and glass electrode assembly was used for *p*H measurements.

Results and Discussion

Addition of the reagent (QAAc) solution to palladium(II) solution resulted in an instant colour. However, 5–10 mins, warming was necessary for the attainment of maximum colour. The complexes of QAAc with palladium were found to be insoluble in aqueous solution, but soluble in 75% v/v (methanol : water) mixture. The complexes were extractable in many water immissible organic solvents. However, chloroform was used for the purpose, as the absorbance was maximum and remained constant for at least five to six hrs.

Spectral Characteristics

Series of solutions containing palladium(II) ($4 \times 10^{-5} M$) and QAAc ($6 \times 10^{-4} M$) at different *p*H

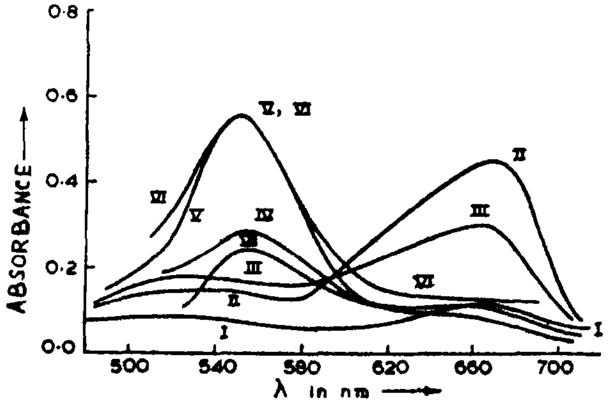


Fig. 1. Absorption Spectra of the Pd-QAAc complexes at Different *p*H.

Conc. of Pd^{2+} Soln. $4 \times 10^{-5} M$
Conc. of QAAc Soln. $6 \times 10^{-4} M$

Curve	*p*H
Curve I at *p*H	1.5
II	2.7
III	4.0
IV	6-0
V	8.0
VI	10.0
VII	11.4

values, were warmed for 5 min. on a steam bath and after extracting them into chloroform, their spectra were recorded against the reagent blanks prepared under identical conditions. It has been found (Fig. 1) that two peaks, one at 670 nm and the other at 550 nm, were obtained at low and high *p*H respectively. The colour of the complex formed at low *p*H (λmax at 670 nm) is green and that formed at high *p*H (λmax at 550 nm) is red, indicating the formation of two different complexes in the system.

Physico-chemical Characteristics of the Complexes

The physico-chemical characteristics of the complexes have been summarised in Table 1.

TABLE 1—PHYSICO-CHEMICAL CHARACTERISTICS OF PD-QAAC COMPLEXES

	Characteristics	Green Complex	Red Complex
1.	λ_{max}	670 nm	550 nm
2.	Workable *p*H range	2.2– 3.0	8.0 – 10.6
3.	Moles of QAAc needed for complexation per mole of metal	2	4
4.	Composition of Complex (M : L)	1 : 1	1 : 2
5.	Validity of Beer's Law (in ppm)	3.2 – 10.65	0 – 7.15
6.	Optimum range for accurate determination of metal (in ppm)	3.5 – 7.4	1.1 – 5.0
7.	Molar extinction (ϵ) Coefficient	1.42×10^4	2.13×10^4
8.	Sandell's Sensitivity (μg Pd/cm^2)	0.0075	0.0049

Recommended Procedure

To a suitable aliquot containing 35 to 70 μg (for green complex) or 12 to 50 μg (for red complex) of palladium(II), add sufficient excess (3 ml of $10^{-3}M$) of QAAc solution, followed by 4 ml of the buffer of requisite *p*H (Table 1). Raise the volume of aqueous phase to 10 ml, keeping 50% v/v methanol concentration. Heat the contents in 50 ml pyrex bottle on a steam bath for 5–10 min. Extract the palladium-QAAc complex in 10 ml of freshly distilled chloroform. Measure the absorbance of the complex *vs.* reagent blank under identical conditions at the corresponding λmax and deduce the amount of palladium from the calibration curve drawn under similar conditions.

Study of the Effect of Diverse ions

The effect of diverse ions was studied by taking requisite amount of palladium (4·24 μg/ml for green complex or 3·39 μg/ml for red complex) and adding different amounts of diverse ions. The tolerance limits for the diverse ions which did not cause deviation of more than $\pm2\%$ in absorbance are given in parentheses below :

Green Complex

The ions I^-, $S_2O_3^{2-}$, CNS^-, CN^-, thiourea and EDTA interfere seriously.

NO_2^-, NO_3^-, Ac^-, BO_3^{3-}, PO_4^{3-} (400); Ox^{2-}, citrate, tartrate, SO_4^{2-} (100); F^-, Br^- (50).

Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, V^{5+}, Pb^{2+}, Ba^{2+}, Sr^{2+}, UO_2^{2+}, Tl^+, Cr^{3+} (1000); Hg^{2+}, Fe^{2+}, and Fe^{3+}, Mn^{2+}, In^{3+} (250); Ag^+, Au^{3+}, Ti^{4+}, Pt^{4+} (100); Cu^{2+} (20); Ru^{3+}, Rh^{3+}, Ir^{3+} (5); Os^{8+} (2).

Red Complex

The ions CN^-, I^-, NO^{2-}, CNS^-, thiourea, $S_2O_3^{2-}$ and F^- interfere seriously.

Br^-, NO_2^-, tartrate (1000); PO_4^{3-} (500); citrate (200); EDTA (150).

Zn^{2+}, Cd^{2+} (40); (Masked with EDTA); Co^{2+}, Ni^{2+}, Cu^{2+}, Hg^{2+} (25); (Masked with EDTA); Tl^+, V^{5+}, W^{6+}, Mo^{6+}, Ag^+, Sr^{2+}, Ba^{2+}, UO_2^{2+}, Ge^{4+}, Al^{3+} (20); Au^{3+} (10); Os^{8+}, Ru^{3+} (5).

Attempts to mask Ir and Fe were unsuccessful.

Determination of Palladium in Alloys

To ascertain the selectivity of the reagent at low *p*H, the method was successfully used for determination of palladium in alloys. Synthetic solutions, similar in composition to that of alloys of palladium were prepared and the amount of palladium was determined following the recommended procedure at low *p*H. The errors in the results obtained, recorded in Table 2 are within $\pm1{\cdot}0\%$.

TABLE 2—DETERMINATION OF PALLADIUM IN SYNTHETIC SOLUTIONS CONTAINING OTHER METALS PRESENT IN ALLOYS

S.No.	Amount of Pd	Amount of other metals present	Amount of Pd found	% error
1.	6.0 ppm	4.0 ppm of Cu^{2+}	6.03	+0.5
2.	6.0 ,,	4.0 ppm of Cu^{2+}	6.02	+0.33
3.	6.0 ,,	4.0 ppm of Ag^+	6.01	+0.16
4.	6.0 ,,	4.0 ppm of Ag^+	5.98	−0.33
5.	6.0 ,,	6.0 ppm of Au^{3+}	6.00	- 0.0
6.	6.0 ,,	6.0 ppm of Au^{3+}	6.00	0.0

Discussion

Although various heterocyclic azo dyes such as PAN, PAR and TAR have proved to be sensitive reagents for the micro determination of palladium, some of the associated metals like copper, silver, gold and cobalt interfere in these methods. In the present study, the interferences of most of the associated metals were found to be negligible even when they were present in four to five times molar excess. The reagent has also been used successfully for the determination of palladium in alloys. As regards the sensitivity of the reagent (0·0075/670 nm, 0·0049/550 nm), it is comparable with the sensitivities

of other heterocyclic azo dyes, viz., PAR[3] (0·0057/440 nm, 0·012/630 nm), TAR[4] (0·013/650 nm), PAN[6] (0·016/610 nm, 0·013/665 nm).

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Lignans and Alkaloids of *Talauma hodgsoni*

S. K. TALAPATRA, S. K. MUKHOPADHYAY and B. TALAPATRA

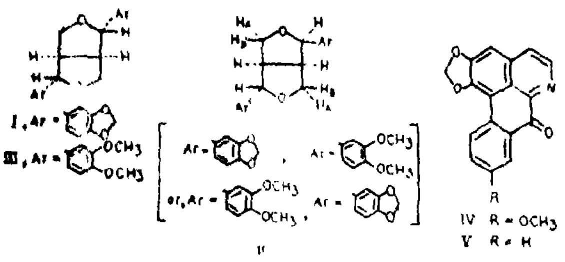
Department of Chemistry, University College of Science, Calcutta-700009

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Three tetrahydrofurofuranoid lignans viz., (+)-sesamin (I), (+)-fargesin (II) and (+)-pinoresinol dimethyl ether (III), and an oxoaporphine alkaloid viz., lanuginosine (IV) along with β-sitosterol have been isolated from the leaves of *Talauma hodgsoni*. The root bark of the plant furnished lanuginosine and liriodenine (V) (an oxoaporphine alkaloid) and β-sitosterol and the tree bark, lanuginosine and β-sitosterol.

THE genus *Talauma* (Fam : Magnoliaceae) comprises about 15 species of trees or shrubs, natives of East Asia, South America and Japan[1]. Up till now only one *Talauma* species, *viz.*, *T. mexicana*, the leaves of which are used as a cardioactive drug[2] and heart stimulant[3,4], has been chemically investigated to yield a new benzylisoquinoline alkaloid, *viz.*, aztequine[3] and three neutral constituents, *viz.*, *p*-hydroxybenzophenone[4], trisomic acid[4] and *d*-quercitol[4] from the leaves, and costunolide, a mixture of two sterols and two coloured compounds from the bark[5]. In the present paper we report the chemical investigation of another *Talauma* species, *viz.*, *T. hodgsoni* H.f and T[1], a lofty evergreen tree growing in the forests of Sikkim Himalayas and Khasia hill at an altitude of 1200–1500 m.

Extensive chromatography of the different fractions of the extractives of *T. hodgsoni*, collected from Darjeeling, resulted in the isolation of three tetrahydrofurofuranoid lignans *viz.*, (+)-sesamin (I)[6] (yield 0·025%), (+)-fargesin (II)[7] (0·011%) and (+)-pinoresinol dimethyl ether (III)[6] (0·1%) and an oxoaporphine alkaloid, *viz.*, lanuginosine (IV)[8,9] (0·006%) along with β-sitosterol (0·007%) from the leaves, while the root bark furnished lanuginosine (0·005%), liriodenine (V)[9,10] (0·004%) (oxoaporphine alkaloid) and β-sitosterol (0·005%); the tree bark



afforded lanuginosine (0·005%) and β-sitosterol (0·004%). The present isolation of (+)-fargesin constitutes its second occurrence in nature, the first isolation being from the flower buds of *Magnolia fargesii*[7]. Although the relative configuration of (+)-fargesin was settled[7] as II, its absolute configuration still remains to be settled.

(+)-Sesamin was identified by direct comparison (co-TLC, IR and Mass spectra) with an authentic sample of (−)-sesamin[11]. Structures of the two other lignans, (+)-fargesin (II) and (+)-pinoresinol dimethyl ether followed from their optical and spectral data (UV, IR, PMR and MS) (*vide* Experimental) which corresponded well with those reported in the literature[7]. Lanuginosine (IV) and liriodenine (V) and β-sitosterol were also identified by direct comparison with the respective authentic samples.

Experimental

Extraction

Dried and powdered leaves (450 g) of *Talauma hodgsoni* were soxhletted with petroleum ether (60°–80°) and $CHCl_3$ respectively; while the root bark (500 g) and tree bark (450 g) were soxhletted with $CHCl_3$. Each of the extracts was separated into basic and neutral fractions in the usual way.

Each of the neutral isolates was chromatographed over silica gel and the basic portions over Brockman alumina (neutral grade), elution being carried out with solvents and solvent mixtures of increasing polarity.

Neutral Constituents

(+)-*Sesamin* (*I*) : The residue obtained from the benzene eluate fractions of the main chromatogram of the neutral portion of the petroleum ether extract of the leaves on rechromatography afforded (+)-sesamin (I), crystallising from petroleum ether-$CHCl_3$ mixture in colourless needles (yield 0·005%), m.p. 121–122°, $[\alpha]_D$ +62·1° (*c* 0·84, $CHCl_3$).

Benzene eluate fractions of the neutral part of the $CHCl_3$ extract of the leaves on similar treatment afforded an additional amount of (+)-sesamin (yield 0·02%).

(+)-*Fargesin* (*II*) : Benzene-$CHCl_3$ (1 : 1) eluate fraction of the above main column upon several rechromatographies afforded (+)-fargesin, crystallised from petroleum ether-$CHCl_3$ mixture as colourless needles (yield 0·004%), m.p. 132–133°, $[\alpha]_D$ +122·2° (*c* 0·73, $CHCl_3$); UV : λ_{max}^{EtOH} (log ε) : 230 (3·84),

283 (3·57); IR : ν_{max}^{KBr} (cm^{-1}) 1613, 1595, 1504 (aromatic), 1080 (dihydrofuran ring) and 923-O-CH_2-O-. PMR (100 MHz, $CDCl_3$, δ) : 2·90 (1H, *m*, H-1); 4·85 (1H, *d*, J = 5 Hz, H-2); 4·43 (1H , *d*, J = 7Hz, H-6); 3·14–3·48 (2H, *m*, H_A-4 and H-5); 3·67–4·0 (2H, *m*, H_B-4, $H_{A'}$-8); 4·08–4·17 (1H, *m*, $H_{B'}$-8); 3·88 (6H, *s*, two OCH_3); 5·92-O-CH_2-O-6·78–6·92 (6H, *m*, aromatic protons). MS (m/e, % base peak) : 370(90·1, M^+), 340(2),339(10),220(4),219(9·8),204(12·2), 203(23·7), 194(11), 178(16), 177(48·3),166(28),165(43·4), 161(27·1), 151(36), 149(100), 137(9), 135(54·9), 121(13). $CHCl_3$-extract of the leaves afforded upon chromatography a further amount of (+)-fargesin (yield 0·007%).

(+)-*Pinoresinol dimethyl ether* (*III*) : The residue obtained from the $CHCl_3$-MeOH (95 : 5) eluate fractions of the main chromatogram afforded on rechromatography (+)-pinoresinol dimethyl ether (III) (yield 0·055%), crystallised from petroleum ether-$CHCl_3$ mixture as colourless needles, m.p. 99°, $[\alpha]_D$ +68·1° (*c* 0·809, $CHCl_3$); UV : λ_{max}^{EtOH} (log ϵ) : 228(3·98), 280(3·52); IR : ν_{max}^{KBr} (cm^{-1}) 1600, 1585 and 1500 (aromatic), 1055 (dihydrofuran ring); PMR (100 MHz, $CDCl_3$, δ) : 3·1 (2H, *m*, H-5 and H-1); 3·72–3·98 (2H, *m*, exo-protons at C-8 and C-4); 3·80 (6H, *s*, two OCH_3); 3·82 (6H, *s*, two OCH_3); 4·15–4·4 (2H, *m*, endo-protons at C-8 and C-4); 4·73 (2H, *d*, J = 5 Hz, H-6 and H-2); 6·83–6·92 (6H, *m*, aromatic protons); MS (m/e, % base peak) : 386 (100, M^+), 356(2·6), 355(8), 220(8·2), 219(20), 205(12), 194(16), 177(75), 166(4·08), 165(90), 151(66), 138(23), 137(7·5). Neutral portion of the $CHCl_3$-extract upon similar treatment afforded a further amount of the same lignan (yield 0·045%).

β-Sitosterol : Benzene eluate portion of the main chromatogram of the neutral fractions of the leaves (both the petroleum ether and $CHCl_3$-extracts) and root- and tree-bark ($CHCl_3$ extracts) afforded β-sitosterol, crystallised from $CHCl_3$-MeOH in flakes (yield : leaves—0·007%, root bark—0·005% and tree bark—0·004%), m.p., 137°, $[\alpha]_D$ −34° (*c* 0·62, $CHCl_3$), acetate m.p. 134°–135°, $[\alpha]_D$ −37·5° (*c* 0·51, $CHCl_3$). Identity of β-sitosterol was confirmed by direct comparison (m.m.p., co-TLC and IR) with an authentic sample.

Basic Constituents

Lanuginosin (*IV*) : Petroleum ether extract of the leaves was found to be devoid of any basic constituents. The $CHCl_3$ eluate portion of the basic fraction of the chloroform extract of the leaves afforded an orange coloured residue, crystallising from $CHCl_3$ as transparent glistening orange crystals (yield 0·006%), m.p. 310°–312° (dec.), M^+ 305; IR : ν_{max}^{KBr} 1650 cm^{-1} (conjugated > C = O), 1600, 1560 and 1495 (aromatic) and 950 (-O-CH_2-O-), and was identified as lanuginosine (IV) by direct comparison (m.m.p., co-TLC [under UV light], IR and Mass spectra) with an authentic sample. Basic fraction of the tree bark on similar treatment afforded the same alkaloid (yield 0·005%).

Liriodenine (*V*) : The basic fraction from the root bark of *T. hodgsoni* showed two close spots under UV light. The constituents could not be separated by chromatography. Repeated fractional crystallisations from $CHCl_3$ afforded the less soluble compound in pure state which was finally purified by chromatography to yield lanuginosine (IV) (yield 0·0032%), identified by direct comparison. From the mother liquor after removal of lanuginosine another yellow oxoaporphine, liriodenine (V) (yield 0·004%) was isolated as the more soluble component, purified by chromatography over alumina and crystallised from petroleum ether-$CHCl_3$ mixture as yellow needles, m.p. 282° (dec.); IR : ν_{max}^{KBr} 1660 cm^{-1} (conjugated > C = O), 1495, 1420 (aromatic), 958 and 942 (-O-CH_2-O-). The compound was identified as liriodenine by direct comparison (m.m.p., co-TLC [under UV light] and IR) with an authentic sample.

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Preparation and Resolution of (±)α-N-Arylamino Acids

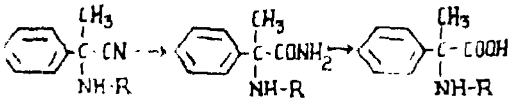
N. K. UNDAVIA, M. L. DHANANI and K. A. THAKER

Dept. of Chemistry, Saurashtra University, Bhavagar 364002

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(±) α-Phenyl-α-N-arylamino propionic acids have been prepared by acid hydrolysis of (±) α-aminonitriles. The (±) acids have been resolved through fractional crystallisation of alkaloidal salts.

(±)-α-AMINOACIDS of proteins have been studied for their physiclogical activity and have high nutritional value, however, few have been resolved. Tiemann and Priest[1] and Knoevenagel[2] prepared (±) phenyl anilino acetic acid by hydrolysis of (±) phenyl anilino acetonitrile, and resolved by McKenzie and Bate[3] by fractional crystallisation of (+) cinchonine salt. The resolution of (±) α-phenyl-α-N-arylamino propionic acids have not been reported. In search of some new drug potential, the preparation and resolution of (±) α-phenyl-α-N-arylamino propionic acids (α-and N substituted alanines) have been undertaken.



(±) α-Aminonitriles[4] prepared from acetophenone, aq. potassium cyanide, glacial acetic acid and aromatic amines were hydrolysed to amides by controlled hydrolysis and amides hydrolysed to acids by dil. sulphuric acid.

(−) Quinine, (+) quinidine, (−) strychnine, and (−) brucine have been tried for the resolution of these (±) amine acids (alanines), out of them (−) brucine was found more suitable. (±) α-Phenyl-α-anilino, (±) α-phenyl-α-(o-toluidino) and (±) α-phenyl-α-naphthylamino propionic acids have been resolved by fractional crystallisation of their (−) brucine salt.

Experimental

Preparation and optical resolution of (±) α-N-arylamino acids

(Compounds prepared were analysed for nitrogen and the nitrogen found agreed with that expected).

(±) α-Phenyl-α-N-arylamino nitrile (5 g) was dissolved in cold conc. H_2SO_4 (10 ml) and kept at room temp. for 48 hrs. It was worked up as usual to get (±) amide and crystallised from ethanol (95%). (±) α-Phenyl-(α-anilino, o-toluidino and 1-naphthylamino) propionamides had the m.p. 124°, 119° and 284° respectively.

(±) Amide (7 g) was dissolved in conc. H_2SO_4 (55 ml) and water (90 ml) added and refluxed for 6–8 hrs. to get (±) acid, crystallised from methanol or methanol pyridine mixed solvent. (±) α-Phenyl-(α-anilino, o-toluidino and 1-napthylamino) propionic acids had the m.p. 247°, 241° and 326° respectively.

(±) Acids obtained were resolved by fractional crystallisation of their 1-brucine salt. α-Phenyl-α-anilino propionic acid has $[\alpha]_D^{30}$ +93·7° and −91·10° (in pyridine) while α-phenyl-α-o-toluidino propionic acid and α-phenyl-α-1-naphthylamino propionic acid has $[\alpha]_D^{30}$ +80·6° and −100·7°, and $[\alpha]_D^{30}$ +156·6° and −159·0° respectively.

Acknowledgement

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Studies in the Cyclohexane Series. Part XVII Two Configurational Isomers of 3,4-Dimethylcyclohexane-1,1-dicarboxylic Acid

R. K. GAUTAM and G. S. SAHARIA

Department of Chemistry, University of Delhi, Delhi-110007

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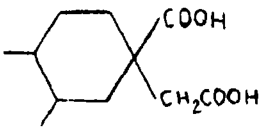
1-Carboxy 3,4-dimethylcyclohexane-1-acetic acid has been prepared by condensing 3,4-dimethylcyclohexanone with ethyl cyanoacetate employing Cope's method to give ethyl 3,4-dimethylcyclohexylidene cyanoacetate and subsequent reaction with ethanolic potassium cyanide followed by hydrolysis. This acid has been separated into two isomers and configurations assigned; each of the isomers has by a series of reactions been degraded to the corresponding 3,4-demethylcyclohexane-1,1-dicarboxylic acid.

THE preparation and assignment of configurations to the two isomeric forms of 4-, 3- and 2-methylcyclohexane-1,1-dicarboxylic acids, being trisubstituted derivatives of cyclohexane, have been reported by Bajaj, Desai and Saharia[1]. Perusal of literature revealed that barring the work on the preparation of 1-carboxy 3,3- and 4,4-dimethylcyclohexane-1-acetic acid[2,3] hardly any analogous work on the tetrasubstituted derivatives of cyclohexane has been reported. The present communication describes the synthesis of isomeric 1-carboxy 3,4-dimethylcyclohexane-1-acetic acids and their conversion to the corresponding 3,4-dimethylcyclohexane-1,1-dicarboxylic acids.

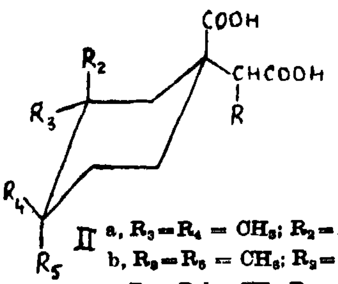
3,4-Dimethylcyclohexanone required for the work was obtained by the catalytic reduction of the corresponding xylenol followed by oxidation which predominantly (97·6%) possesses the cis-configuration.[4]

the first method, 3,4-dimethylcyclohexanone has been condensed with ethyl cyanoacetate following Cope's method[5] and the unsaturated ester so obtained on reaction with ethanolic potassium cyanide followed by hydrolysis furnished 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid (I) as a mixture of two acids having m.p. 105–28°. While in the other, the condensation of 1-hydroxy-1-cyano-3,4-dimethylcyclohexane with ethyl sodiocyanoacetate was carried out to give 1-cyano-3,4-dimethylcyclohexane-1-cyanoacetate. This dicyanoester on hydrolysis with concentrated hydrochloric acid furnished the acid (I), m.p. 105–27°. This acid has been separated into two isomers A, m.p. 181° and B, m.p. 160° by fractional crystallisation from ethyl acetate-pet. ether and benzene-pet. ether which were obtained in the ratio of 1 : 3.

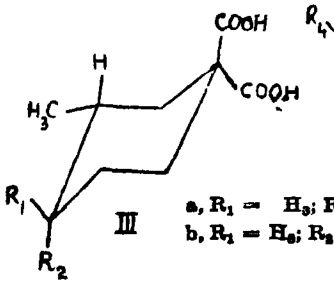
In order to assign configurations to the two isomers, each was converted into its ethyl ester and their



I



II a, $R_3 = R_4 = CH_3$; $R_2 = R_5 = H$
b, $R_3 = R_5 = CH_3$; $R_2 = R_4 = H$
c, $R_2 = R_4 = CH_3$; $R_3 = R_5 = H$
d, $R_2 = R_5 = CH_3$; $R_3 = R_4 = H$



III a, $R_1 = H_3$; $R_2 = H$
b, $R_1 = H_3$; $R_2 = CH_3$

1-Carboxy 3,4-dimethylcyclohexane-1-acetic acid has been synthesized by two different routes and in

b.ps and refractive indices recorded. Out of the two groups $-CH_2COOH$ and $-COOH$ in I at C_1, the

former being bulkier would occupy the equatorial position in the chair conformation. As a consequence of this four different configurations of the acid I could be represented by II (a, b, c and d; R = H) depending upon whether one or both the methyl groups occupy equatorial or axial positions.

Configuration IIa would be energetically the most favourable and thus stable for both the methyl groups are in equatorial positions as the molecule would be free from any 1,3-diaxial interactions. On the other hand IId will be most unstable because of 1,3-hydrogen-methyl and 1,3-methyl-carboxyl interactions and therefore, this could be ruled out.

Out of the remaining two configurations, IIb and IIc, the latter would distinctly possess higher energy since the methyl group at C-3 and -COOH group at C-1 occupy axial positions and appear on the same side of the ring. Thus, the order of the relative stabilities of the different configurations would be in the order, $a > b > c > d$ and the two isomers *A* and *B* could be considered to have the configurations *a* and *b*.

On the basis of von Auwers-Skita rule as modified by Allinger[4] the isomer *A* (refractive index of the ethyl ester, n_D^{25} 1·4665) is assigned the structure '*a*' in which both the methyl groups assume equatorial positions and the isomer *B* (refractive index of the ethyl ester, n_D^{25} 1·4785) is assigned the structure '*b*' in which the methyl groups at C-3 and C-4 assume equatorial and axial positions respectively.

von Auwers-Skita rule in the case of b.ps of the ethyl esters of isomers Ia and Ib (b.ps Ia—130-1°/1·5 mm; Ib—111°/2 mm) was found to be reversed in accordance with that reported by Eliel and Haber[7] in the case of isomeric methylcyclohexanols, also suggested by van Bekkum and others[8] that the conformational rule should be confined to density and refractive index, since the rule frequently fails for b.p.

Further, assignment of structure '*b*' in preference to '*c*' for the isomer *B* is supported by the observations of Noyce and Dolly[4] that the major transition state contributor in the lithium aluminium hydride reduction of cis-3,4-dimethylcyclohexanone has 3*e*, 4*a* dimethyl configuration.

The configurations assigned receive further support from the nmr spectra of the anhydride of 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid A, m.p. 181° in $CDCl_3$ which gave an intense signal at 0·97δ arising from six methyl protons. Whereas the nmr spectra of the anhydride of the acid B, m.p. 160° showed two signals at 1·03δ and 0·9δ due to methyl protons because axial and equatorial methyl protons absorb at different fields[9].

The isomeric 1-carboxy 3,4-dimethylcyclohexane-1-acetic acids (IIa and IIb; R = H) were degraded to the respective -1,1-dicarboxylic acids according to the procedure of Desai, Hunter and Saharia[1,10]. It was observed that addition of traces of red phosphorus to the brominating mixture already having a crystal of iodine, facilitated the completion of the reaction (2 hours). It may be mentioned that no neutral product was isolated contrary to the early observations[1,10] and it may be probable that prolonged heating for a longer time resulted in the formation of the neutral product.

The yields of 1-carboxy 3,4-dimethylcyclohexane-1-α-bromoacetic acids (IIa and IIb; R = Br) were quantitative and those of the corresponding hydroxy acids (IIa and IIb; R = OH) ranged between 76 to 79%. The structures of the bromo acids and the glycollic acids were confirmed by analytical data, eq. weight determination and I.R. spectral data. The glycollic acids were later oxidised with alkaline potassium permanganate to the respective 3,4-dimethylcyclohexane-1,1-dicarboxylic acids (IIIa and IIIb) in yields of 47–55%. These acids solidified only on keeping in vacuum for over two months followed by trituration with benzene and pet. ether.

Our results regarding the structures of glycollic acids and -1,1-dicarboxylic acids, are in consonance with the observations of Bajaj *et al.*[1], Desai *et al.*[10] thereby further contradicting the claims made by Price and co-workers[11].

Experimental

(a) *Ethyl 3,4-dimethylcyclohexylidene cyanoacetate*

A mixture of 3,4-dimethylcyclohexanone (63 g; 0·5 mole), ethyl cyanoacetate (56·5 g; 0·5 mole), ammonium acetate (4·0 g; 0·05 mole), glacial acetic acid (6·0 g; 0·1 mole) and dry benzene (120 ml) contained in a R.B. flask (500 ml) fitted with a modified Dean and Stark water separator, in turn connected to a reflux condenser, was heated in an oil bath at 120–60°. Water separated out of the mixture was drawn off at intervals and the mixture refluxed for an additional period of two hours after the separation of water had stopped (3 hours). The benzene solution was cooled, washed with water (2×100 ml) and the washings were extracted with benzene (40 ml). The combined benzene extracts after drying and removal of benzene gave ethyl 3,4-dimethylcyclohexylidene cyanoacetate, b.p. 160–3°/8–9 mm. n_D^{28} 1·4735. (Yield : 89·6%). (Found : C, 70·5; H, 8·5. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·6%). I.R. ν_{max}^{film} 1720 cm^{-1}; νC = O (α, β-unsaturated ester); 1600 cm^{-1}: νC = C, 2250 cm^{-1}; νC ≡ N, λ_{max} 235 mμ.

1-*Carboxy 3,4-dimethylcyclohexane-1-acetic acid (I)*

To the solution of ethyl 3,4-dimethylcyclohexylidene cyanoacetate (99·9 g; 0·43 mole) in rectified spirit was gradually added potassium cyanide (58·5 g; 0·9 mole) in water (100 ml) with shaking and cooling, and the contents left at room temperature for 96 hrs. Alcohol was distilled off at the pump, the residue cooled and acidified with conc. hydrochloric acid when an oily layer separated out. This was extracted with ether and the residue after the removal of ether was refluxed with conc. hydrochloric acid (200 ml) on a sand bath for 90 hrs; a semi-solid product which had settled down was separated by decantation and washed with water. This was dissolved in aq. sodium hydroxide (10%) and heated under reflux until the evolution of ammonia had ceased (15 hrs.)

and the alkaline solution on acidificaton deposited an oil which solidified after keeping at room temperature for four days and had m.p. 105–27°. (Yield : 81%).

(b) *Synthesis of* 1-*hydroxy*-1-*cyano*-3,4-*dimethylcyclohexane*

To a mixture of 3,4-dimethylcyclohexanone (32 g; 0·25 mole) and potassium cyanide (16·3 g; 0·25 mole) in water (100 ml) was slowly added, with stirring, dilute sulphuric acid (167 g; 30% by weight) and temperature maintained below 20°. After two hours, the contents were extracted with ether, the ethereal solution dried over anhydrous magnesium sulphate and the solvent removed, the residue on distillation with two drops of conc. sulphuric acid gave 1-hydroxy-1-cyano-3,4-dimethylcyclohexane, b.p. 129°–30°/5–6 mm. n_D^{30} 1·4570. (Yield : 73%). (Found : C, 70·3; H, 9·7. $C_9H_{15}ON$ requires C, 70·5, H, 9·8%). I.R. ν_{max}^{film} 2265 cm^{-1}; νC ≡ N; 3605 cm^{-1}; νO-H (alcoholic monomeric).

Ethyl 1-*cyano*-3,4-*dimethylcyclohexane*-1-*cyanoacetate*

1-Hydroxy-1-cyano-3,4-dimethylcyclohexane (22·9 g; 0·15 mole) was slowly added, with cooling and stirring, to the sodio derivative of ethyl cyanoacetate prepared from ethyl cyanoacetate (16.95 g; 0·15 mole) by the action of sodium ethoxide (sodium 3·45 g; 0·15 mole and absolute alcohol 55 ml). The mixture after keeping at room temperature for 24 hrs. was diluted with water and acidified when an oily layer separated out. After working up in the normal manner, pure 1-cyano-3,4-dimethylcyclohexane-1-cyanoacetate had b.p. 160°/5 mm. n_D^{28} 1·4696. (Yield : 61·6%). (Found . C, 67·5; H, 8·0. $C_{14}H_{20}O_2N_2$ requires C, 67·7; H, 8·1%). I R. ν_{max}^{film} 2260 cm^{-1}; νC ≡ N; 1730 cm^{-1} : νC = O of ester.

1-*Carboxy* 3,4-*dimethylcyclohexane*-1-*acetic acid* (*I*)

Ethyl 1-cyano 3,4-dimethylcyclohexane-1-cyanoacetate (20 g) was hydrolysed with conc. hydrochloric acid as described earlier and the crude acid had m.p. 105–28°. (Yield : 83·1%).

Separation of isomeric 1-*carboxy* 3,4-*dimethylcyclohexane*-1-*acetic acids*

The above acid 70 (g) was finely powdered and refluxed with petrol (60°–80°) containing a small quantity of benzene for an hour, the residue m.p. 167–75° on further treatment with benzene and crystallisation from ethyl acetate-benzene gave 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid, (IIa) as thick clusters of white needles m.p. 181°. (Found : C, 61·6; H, 8·3; equiv., 106·8. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%; equiv. 107·0—dibasic). I.R. ν_{max}^{Nujol} 1710 cm^{-1}. Anhydride, m.p. 104·5°, Anilic acid, m.p. 165°, *p*-Tolylamic acid, m.p. 185°, *p*-Chloroanilic acid, m.p. 178°, *m*-Nitroanilic acid, m.p. 178°.

The petrol and benzene mother liquors were combined, concentrated to half its total volume and on standing deposited a solid m.p. 140–7°. This on treatment with benzene gave a residue melting at 173–5° which on repeated crystallisations gave more quantity of acid IIa. The final mother liquor on further concentration deposited a fraction melting at 153–7°; on two crystallisations from benzene, 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid, IIb was obtained in white cubes and had m.p. 160°. (Found : C, 61·5; H, 8·4; equiv., 106·7. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%; equiv., 107·0—dibasic). I.R. ν_{max}^{Nujol} 1705 cm^{-1}. Anhydride, b.p. 183–4°/10–11 mm., Anilic acid, m.p. 160°, *p*-Tolylamic acid, m.p. 193°, *m*-Nitroanilic acid, m.p. 168°. Mixed m.p. of the acid IIa, m.p. 181° with the acid Ib, m.p. 160° in the ratio 2 : 1 was depressed to 142–6°.

Bromination of 1-*carboxy* 3,4-*dimethylcyclohexane*-1-*acetic acid IIa. m.p.* 180° (IIa, R = Br)

Powdered phosphorus pentachloride (11·5 g; 0·055 mole) and 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid (5·35 g; 0·025 mole) were mixed together and the mixture heated under reflux for 6 hrs. Bromine (5·73 g; 0·0275 mole) was added to the cooled contents during two hours and left overnight at room temperature with a crystal of iodine and a pinch of red phosophorus. After exposing the contents to U.V. light for 6 hrs, the reaction mixture was heated in an oil bath at 55–60° for 24 hrs. and poured into anhydrous formic acid (98%; 50 ml) with constant stirring. After the initial reaction had subsided, the contents were heated on a water bath until the decomposition was complete (2 hrs.). The solid which separated out after keeping overnight, was filtered, washed with petrol and on crystallisation from benzene-petrol (40–50°) 1-carboxy 3,4-dimethylcyclohexane-1-α-bromoacetic acid was obtained in white cubes and had m.p. 149°. (Yield : 81·9%). (Found : C, 45·0; H, 5·6; Br, 27·2; equiv., 146·1. $C_{11}H_{17}O_4Br$ requires C, 45·1; H, 5·8; Br, 27·3; equiv., 146·5—dibasic). I.R. ν_{max}^{Nujol} 1700 cm^{-1} : νC = O of acid and 1720 cm^{-1} : νC = O of α-halogenated acid.

1-*Carboxy* 3,4-*dimethylcyclohexane*-1-*glycollic acid* (IIa; R = OH)

The above α-bromo acid (5 g) was neutralized with aqueous sodium carbonate (2*N*) and the solution refluxed on a sand bath for 6 hr. The reaction mixture was cooled, acidified with conc. hydrochloric acid and extracted with ether. The residue, after the removal of ether, on trituration with petrol (60–80°) containing a few drops of benzene gave a colourless solid melting at 152–5°. This was crystallised from benzene-pet. ether (60°–80°) in white plates and pure 1-carboxy 3,4-dimethylcyclohexane-1-glycollic acid had m.p. 158°. (Yield : 78·9%). (Found : C, 57·1; H, 7·7; equiv. 114·8. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·8%; 115·0 dibasic). I.R. ν_{max}^{Nujol} 1705 cm^{-1} : νC = O of acid; 3625 cm^{-1}: νO-H.

3,4-*Dimethylcyclohexane*-1,1-*dicarboxylic acid* (IIIa)

The solution of 1-carboxy 3,4-dimethylcyclohexane-1-glycollic acid (2·3 g) in water was neutralised with aqueous barium hydroxide (N/20) and potassium permanganate (4·5 g in water, 450 ml) was slowly added during 5 hrs. while the mixture kept constantly stirred. The contents were allowed to stand at room

temperature for 15 hrs, and the unreacted permanganate was destroyed by passing sulphur dioxide. The ppted manganese dioxide was filtered off, the filtrate concentrated to a small bulk, the alkaline solution acidified with conc. hydrochloric acid, saturated with ammonium sulphate and continuously extracted with ether for 10 hrs. The ethereal solution was dried over anhydrous magnesium sulphate, ether recovered and the residue kept in vacuum for two months; on trituration with benzene-petrol (60–80°) a colourless solid, m.p. 150–2° was obtained. On crystallisation from ethyl acetate petrol (60–80°), 3,4-dimethylcylclohexane-1, 1-dicarboxylic acid, m.p. 155° was obtained in colourless cubes. (Yield : 55%). (Found : C, 59·8; H, 7·9; equiv., 99·7; $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; equiv., 100·0—dibasic). Mixed m.p with 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid IIa, m.p. 181° in the ratio 1 : 1 was depressed to 130–40° and with the acid IIb, m.p. 160° was pdepressed to 141–3°. I.R. ν_{max}^{Nujol} 1715 cm^{-1}. Its diethyl ester distilled at 132/3 mm. n_D^{25} 1·4410.

1-*Carboxy 3,4-dimethylcyclohexane*-1-*α-bromo acetic acid* (IIb; R = Br) prepared in the manner followed in the case of isomer IIa had m.p. 146–7° (Yield : 84·6%). (Found : C, 45·0; H, 5·5; Br. 27·1%; equiv., 145·9. $C_{11}H_{17}O_4Br$, requires C, 45·1; H, 5·8; Br, 27·3%; equiv., 146·5—dibasic). I.R. ν_{max}^{Nujol} 1700 cm^{-1} : $\nu C = O$ of acid; 1715 cm^{-1} : $\nu C = O$ of α-halogenated acid.

1-*Carboxy 3,4-dimethylcyclohexane*-1-*glycollic acid* (IIb; R = OH) had m.p. 152–3°. (Yield : 76·1%). (Found : C, 57·2; H, 7·5; equiv., 114·6. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·8%; equiv., 115·0—dibasici. I.R. ν_{max}^{Nujol} 1707 cm^{-1} : $\nu C = 0$ of acid; 3630 cm^{-1} : νO-H.

3,4-*Dimethyl cyclohexane*-1,1-*dicarboxylic acid* (IIIb) m.p. 172° was prepared following the method adopted as for the isomer IIIa. (Yield : 47·5%). (Found : 59·7; H, 8·0; equiv., 99·7. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%; 100·0—dibasic). Mixed m.p. with 1-carboxy 3,4-dimethycyclohexane-1-acetic acid IIb, m.p. 160° *in the ratio of 1 : 1* was depressed to 145–50°, while the mixed IIIa m.p. with 3,4-dimethycyclohexane-1,1-dicarboxylic acid, IIIa m.p. 155° in the ratio of 2 : 1 was depressed to 140–7°. I.R. ν_{max}^{Nujol} 1721 cm^{-1}. Its diethyl ester distilled at 115°/4 mm. n_D^{25} 1·4525.

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Chemical Investigation of the Leaves of *Xanthium strumarium* Linn

N. P. S. BISHT* and RANBIR SINGH**

Department of Chemistry, J. V. College, Baraut (Meerut)

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Isohexacosane, chlorobutanol, stearyl alcohol, β-sitosterol, ε-Sitosterol and palmitic acid have been isolated from the leaves of *Xanthium strumarium* Linn. The isolation of isohexacosane and chlorobutanol have been reported for the first time from natural source.

XANTHIUM terumarium Linn (Family : Compositae) is a medium size herb which grows throughout the hot parts of India. This plant is reputed for its extensive medicinal importance. The whole plant is used as diaphoretic, sedative, sudorific and considered useful in long standing malaria. The root of the plant is used as bitter tonic and in the treatment of cancer and strumous diseases, while the fruits as cooling, demulcent and given in small-pox[1].

Bhakuni *et al*[2] reported the isolation of β-sitosterol, γ-sitosterol, ε-sitosterol and the component fatty acids, palmitic, stearic, oleic and linoleic from the *fruits* of *Xanthium strumarium*. They also isolated strumaride, sugars; tartaric, succinic, malic, fumaric acids; amino acids, proteins and inorganic salts from the same source. Tsukamoto *et al.*[3] isolated β-sitosterol, stigmasterol or campestrol from the *seeds* of this plant. The other constituents isolated by different workers from the plant material were Xanthatin[4], Xanthinin[4,5], Xanthumin[6], Xanthanol and isoxanthanol[7], 8-(Δ^{3}-isopentenyl)-5 : 7 : 3′ : 4′-tetra hydroxy flavone[8], caffeic acid and cinarin[9] and essential oil[10].

The present communication reports the isolation of isohexacosane, chlorobutanol, stearyl alcohol, β-sitosterol, ε-sitosterol and plamitic acid from the *leaves* of Indian *X. strumarium*.

The petroleum ether (60–80°) extract of the leaves of the plant *Xanthium strumarium* Linn after column chromatography yielded a hydrocarbon and the pasty mass. The hydrocarbon $C_{26}H_{54}$, m.p. 60–61° have been characterised as isohexacosane by spectral analysis. The pasty mass was saponified, the unsaponifiable material was extracted with ether, and subjected to steam distillation after removing the solvent, which gave a white compound (purified by sublimation) $C_4H_7Cl_3O$, m.p. 96·5–97° and have been characterised as chlorobutanol by comparison of m.p., UV, IR spectra etc. The chlorine was also estimated[11] in the dry leaves of the plant and was found to be 1·16±0·05%. The material left after steam distillation, on column chromatography yielded four compounds A, B, C and D. The compound A, $C_{18}H_{38}O$, m.p. 59–60°, was identified as stearyl alcohol by its m.m.p., IR spectrum and preparation of *p*-nitro benzoate, m.p. 64–65°. The compound B, $C_{29}H_{50}O$, m.p. 134–35°, was found to be β-sitosterol by m.m.p., IR and NMR spectra and preparation of its acetate, m.p. 120–21°. The compound C, $C_{29}H_{50}O$, m.p. 144–45°, identified as ε-sitosterol by m.m.p., IR spectrum and preparation of its acetate, m.p. 126–27°. The compound D, m.p. 156–57° could not be identified. The saponified part yielded palmitic acid $C_{16}H_{32}O_2$, m.p. 61–62°, identified by m.m.p., IR spectrum and preparation of its derivatives.

Experimental

The finely powdered air dried leaves of the plant (2 kg) collected from Baraut locality were extracted exhaustively with petroleum ether (60°–80°) in a soxhlet extractor. The extract was concentrated and chromatographed over Brockman alumina (250 g, deactivated with 10% AcOH) with petroleum ether and its mixture with benzene with increasing polarity, the ratio of the latter was increased slowly.

Isohexacosane

The petroleum ether–benzene (1 : 1) fraction furnished white solid, crystallised from petroleum ether in white granules (1 g), m.p. 60–61°, (Found : C, 85·02; H, 14·87%; Calc. for $C_{26}H_{54}$, C, 85·24; H, 14·75%).

Chlorobutanol

The benzene eluent was concentrated to dryness and hydrolysed with 0·5*N* alcoholic KOH on a steam bath. The unsaponifiable material was extracted with ether and solvent was distilled off. The amorphous residue thus obtained on steam distillation gave a white compound, which was

* Correspondence to this author.

** Present address : Principal, Sri Aurobindo College, University of Delhi, Delhi.

finally purified by sublimation, colourless needles (2·5 g), m.p. 96·5–97°; (Found : C, 26·93; H, 3·91; Cl, 59·77%; Calc. for $C_4H_7Cl_3O$, C, 27·04; H, 3·98; Cl, 59·94%). It was characterised as chlorobutanol (β : β : β-trichloro-*tert*. butyl alcohol) by direct comparison with an authentic sample, m.m.p., Co-TLC and Co-IR.

The material left after steam distillation was extracted with chloroform and rechromatographed over deactivated alumina with petroleum ether-benzene (1 : 1) and benzene, which yielded four compounds A, B, C and D. The compounds B, C and D gave a positive test for plant sterols.

Stearyl alcohol (*Compound A*) :

The compound A was crystallised from EtOH in white leaflets (0·9 g), m.p. 59–60°; (Found : C, 79·76; H, 14·23%; Calc. for $C_{18}H_{38}O$, C, 80·0; H, 14·07%). It was identified as stearyl alcohol by m.m.p. and preparation of its *p*-nitro benzoate (by the *p*-Nitrobenzoyl chloride/Py method, crystallised from MeOH as colourless crystals), m.p. 64–65°.

β-Sitosterol (*Compound B*)

The compound B was crystallised from MeOH in colourless plates (235 mg), m.p. 134–35°; (Found : C, 83·86; H, 12·22%; Calc. for $C_{29}H_{50}O$, C, 84·06; H, 12·08%). It was identified as β-sitosterol and the identity was confirmed by m.m.p., NMR spectrum and preparation of its acetate (by the Ac_2O/Py method, crystallised from MeOH as colourless flakes), m.p. 120–121°.

ε-Sitosterol (*Compound C*)

The compound C was crystallised from EtOAc-Ether (1 : 1) in colourless needles (150 mg), m.p. 144–145°; (Found : C, 83·90; H, 12·10%; Calc. for $C_{29}H_{50}O$, C, 84·06; H, 12·08%); ν_{max} (Nujol) 3400–3250, 1060, 1050, 1020, 970, 836, 800 and 715 cm^{-1}. It was identified as ϵ-sitosterol by m.m.p. and preparation of its acetate (by the Ac_2O/Py method, crystallised from MeOH : $CHCl_3$ (1 : 1) as colourless needles), m.p. 126–127°.

Compound D

The compound D, m.p. 156–157°, gave positive Liebermann-Burchard test but could not be identified owing to lack of experimental evidences.

Palmitic acid

The saponified part was worked up as usual. This on chromatography over alumina yielded palmitic acid, white crystals (EtOH) (1·5 g), m.p. 61–62°, (Found : C, 74·82; H, 12·64%; Calc. for $C_{16}H_{32}O_2$, C, 75·00; H, 12·50%). The identity of the compound was confirmed by m.m.p. and preparation of amide m.p 105–106° and anilide m p 88–89° in the usual way.

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Kinetics and Mechanism of Ag^+ Catalysed Oxidation of Dicarboxylic Acids by Peroxydisulphate Ion-Oxidation of Malonic, Succinic and Adipic Acids

R. N. MEHROTRA, A. K. SHUKLA and S. P. SRIVASTAVA*
Chemical Laboratories, University of Roorkee, Roorkee

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The kinetics of Ag^+ catalysed oxidation of three typical dicarboxylic acids—succinic acid, adipic acid and malonic acid by peroxydisulphate ion in aqueous medium has been investigated. In all the three cases, the reaction is found to be first order in $S_2O_8^{2-}$ and in the catalyst Ag^+ and zero order in substrate. However, the first order rate constant is found to be slightly dependent on the concentration of $S_2O_8^{2-}$ as well as on the concentration of substrate which may be ascribed to trace impurity. The reaction exhibits negative salt effect of the exponential type and also shows specific inhibitory effect. The energy parameters determined in each case show a close similarity. The reaction is inhibited by traces of allyl acetate. The products of oxidation identified in each case are: Succinic acid—tartaric acid and oxalacetic acid; Malonic acid—meso-oxalic acid, formaldehyde and CO_2; Adipic acid—monoketo adipic acid and levulinic acid. Considered with the above observations, a radical chain mechanism has been proposed and the corresponding rate expression derived.

PEROXYDISULPHATE ion has been used to oxidise a number of organic compounds and the kinetics of these reactions has been the subject of study of a large number of workers, as reviewed by House[1]. However, a review of literature shows that, inspite of a large number of work, there is lack of general agreement on the mechanism of many of these reactions e.g., for the oxidation of the first dicarboxylic acid-oxalic acid. A survey of literature shows that little work appears to have been done on the kinetics of oxidation of higher dicarboxylic acids by $S_2O_8^{2-}$, the only study reported being the kinetic study of uncatalysed oxidation of malonic acid[2]. Hence a detailed kinetic study of the Ag^+ catalysed oxidation of three dicarboxylic acids—malonic, succinic and adipic acids by peroxydisulphate ion has been carried out by us, the results of which are reported in this paper.

Experimental

$K_2S_2O_8$, $AgNO_3$, substrates and other reagents used were either of E.Merck (G.R.) or B.D.H. (AnalaR) grade and $K_2S_2O_8$ was used after recrystallization with double distilled water. The progress of reaction was followed by estimating unreacted peroxydisulphate, using iodometric method given by Szabo, Csyani and Galiba[3], as modified by Khulbe and Srivastava[4].

Stoichiometry and product analysis

It is found that two moles of $K_2S_2O_8$ are consumed by one mole of the acid according to the stoichiometric equations:

$$CH_2\langle{}^{COOH}_{COOH} + 2S_2O_8^{2-} + H_2O \xrightarrow{Ag^+} O=C\langle{}^{COOH}_{COOH} + 4HSO_4^-$$

malonic acid → meso-oxalic acid (I)

$$\xrightarrow{Ag^+} HCHO + 2CO_2 + 4HSO_4^-\quad \text{(II)}$$

$$\begin{matrix} CH_2\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{matrix} + 2S_2O_8^{2-} \xrightarrow{2H_2O + Ag^+} \begin{matrix} HO\text{-}CH\text{-}COOH \\ | \\ HO\text{-}CH\text{-}COOH \end{matrix} + 4HSO_4^-$$

succinic acid → III tartaric acid

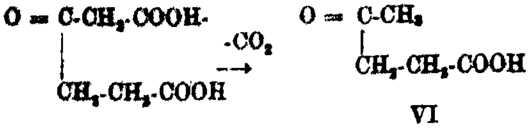
$$\xrightarrow{H_2O + Ag^+} \begin{matrix} O=C\text{-}COOH \\ | \\ CH_2\text{-}COOH \end{matrix} + 4HSO_4^-$$

oxal acetic acid IV

$$\begin{matrix} CH_2\text{-}CH_2\text{-}COOH \\ | \\ CH_2\text{-}CH_2\text{-}COOH \end{matrix} + 2S_2O_8^{2-} + H_2O \xrightarrow{Ag^+} \begin{matrix} O=C\text{-}CH_2\text{-}COOH \\ | \\ CH_2\text{-}CH_2\text{-}COOH \end{matrix} + 4HSO_4^-$$

Adipic acid → mono keto adipic acid

Mono keto adipic acid undergoing decarboxylation to give levulinic acid (VI) accompanied by brisk evolution of CO_2.



VI
(Levulinic acid)

Products I, IV, V and VI were identified by preparation of their respective 2, 4-dinitro phenyl hydrazones, while formaldehyde(II) was detected by conventional tests as well as by preparation of its hydrazone. The presence of oxal acetic acid (IV) was also confirmed by thin layer chromatography[5] and two dimensional chromatography[6]. The formation of tartaric acid (III) was detected by paper chromatography and confirmed by ammonium vanadate and sodium nitroprusside tests.

Order of reaction

In each case, the reaction, for any kinetic run, is found to be first order in peroxydisulphate and zero order in organic acids, as evaluated by Vant Hoff differential method by employing initial rates determined by 'Plane mirror method'[7]. The specific rate is found to be first order in Ag^+ concentration in all the three cases. However, the first order rate constant is found to decrease slightly with increase in $K_2S_2O_8$ concentration at constant ionic strength and constant K^+ concentration (Table 1).

TABLE 1—EFFECT OF VARIATION OF $K_2S_2O_8$ AT CONSTANT IONIC STRENGTH

[Substrate] = $0.01M$; [$AgNO_3$] = $0.001M$; Temp. = 35°

$K_2S_2O_8$ (M)	K_2SO_4 (M)	$k' \times 10^3$ (min^{-1})	Malonic acid $k \times 10^3$ (min^{-1})	Succinic acid $k \times 10^3$ (min^{-1})	Adipic acid $k \times 10^3$ (min^{-1})
0.01	0.04	1.03	1.62	1.04	0.95
0.02	0.03	0.92	1.48	1.00	0.90
0.03	0.02	0.90	1.40	0.97	0.87
0.04	0.01	0.87	1.34	0.94	0.84
0.05	0.00	0.80	1.30	0.93	0.83

k' = specific rate for self decomposition.
k = net specific rate for oxidation of organic substrate.

Similarly, increase in concentration of the reductant slightly decreases the specific rate in all the three cases (Table 2).

Similar results have been observed by other workers also in the case of other substrates[8–10]. This slight decrease in specific rate with increase in substrate concentration may be due to an alternative equilibrium process $H^+ + S_2O_8^{2-} \rightleftharpoons HS_2O_8^-$ taking place preferentially at lower pH and thus affecting the equilibrium process with Ag^+. Since this slight dependence of rate constant on the concentration of the oxidant as well as that of substrate has been observed at constant ionic strength and constant K^+ concentration, the possible cause for it may also be traced to trace impurities present in the reactants[11]. The dependence of the specific rate on the concentration of the oxidant as well as on the substrate concentration suggests that the reaction follows a radical mechanism, which is supported by the fact that allyl acetate, a radical scavenger, inhibits the rate of reaction in all the three cases; the decrease in rate by the addition of $0{\cdot}001M$ allyl acetate being nearly 10%, 13% and 20% for succinic acid, adipic acid and malonic acid oxidation respectively.

TABLE 2—EFFECT OF VARIATION OF SUBSTRATE CONCENTRATION

[$K_2S_2O_8$] = $0.01M$; [$AgNO_3$] = $0.001M$; Temp. = 35°
$k' = 1.04 \times 10^{-3}$ min^{-1}.

Substrate (M)	Malonic acid $k \times 10^3$ (min^{-1})	Succinic acid $k \times 10^3$ (min^{-1})	Adipic acid $k \times 10^3$ (min^{-1})
0.01	1.59	1.38	1.17
0.02	—	1.30	0.96
0.03	1.27	—	0.81
0.04	—	1.25	0.71
0.05	1.16	—	0.64
0.06	—	1.20	—
0.07	1.08	—	—
0.08	—	1.18	—
0.10	1.00	—	—

Salt effect

In all the cases, the salt effect (as determined by using K_2SO_4 as neutral salt) is negative and of primary exponential type suggesting that the rate determining process in all the three cases is between two oppositely charged ions.

The specific inhibitory effect of different cations followed a similar order in all the three reactions

$$K^+ > Na^+ > Zn^{++} > Mg^{++} > Al^{+++}$$

Thermodynamic parameters

By a study of the three reactions at five different temperatures (30°–50°), the energy parameters were evaluated, as presented in Table 3.

A close similarity in the values of energy of activation, frequency factor, free energy of activation and entropy of activation in the three cases points to the fact that the three reactions follow a similar mechanism. A large negative value of entropy of activation has been earlier reported for Ag^+ catalysed redox reactions of $S_2O_8^{2-}$ with other substrates[10,12–16] also. Further a large negative value of entropy of activation indicates that the formation of the activated complex involves a reaction either between two oppositely charged ions or between an ion and a neutral molecule.

Mechanism

In view of the above results and the formation of a complex between Ag^+ and $S_2O_8^{2-}$, as also proposed

by Bekier and Kijowski[12] and later on supported by Chaltykyan and Beileryan[13] for other substrates,

TABLE 2—THERMODYNAMIC PARAMETERS

$[K_2S_2O_8] = [\text{Acid}] = 0.01M$; $[AgNO_3] = 0.001M$

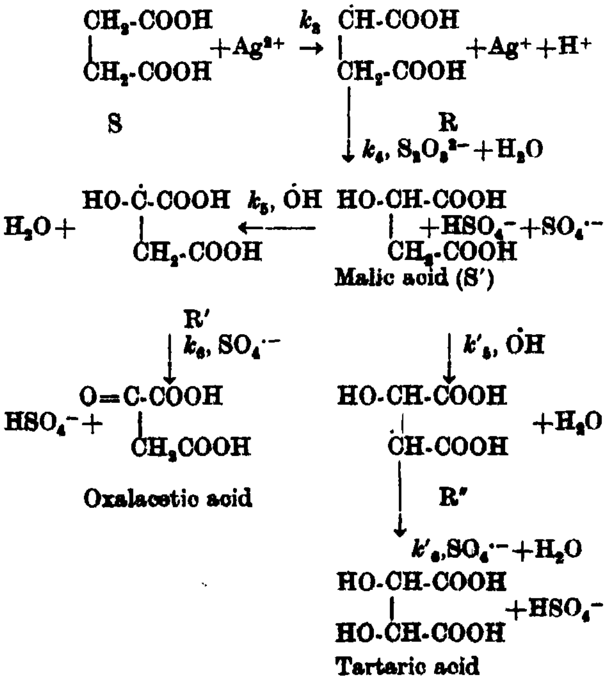
	Temp. °A	$k \times 10^2$ (min^{-1}) Malonic acid	Succinic acid	Adipic acid
	303	—	1.06	—
	308	1.59	1.38	1.17
	313	2.16	1.81	1.40
	318	2.74	2.28	1.98
	323	3.56	3.08	2.48
	328	4.79	—	3.36
Mean values	E (Kcal mole^{-1})	10.7(±0.4)	9.8(±0.5)	10.9(±0.6)
	A×10^{-2} (sec^{-1})	7.15	6.39	10.90
	ΔG≠ (Kcal mole^{-1})	25.0	24.8	25.2
	ΔS≠ (E.U.)	−46.6	−47.8	−46.8

the following mechanism seems reasonable (taking succinic acid as an example) :

$$S_2O_8^{2-} + Ag^+ \overset{K}{\rightleftharpoons} AgS_2O_8^-$$

$$AgS_2O_8^- \xrightarrow{k_1} SO_4^{2-} + SO_4^{\cdot -} + Ag^{2+}$$

$$SO_4^{\cdot -} + H_2O \xrightarrow{k_2} \dot{O}H + HSO_4^-$$



Here it is seen that malic acid formed in stage 4 can react by two alternative paths and because of its immediate conversion into oxalacetic acid and tartaric acid, it is not detected in the reaction mixture by chromatographic analysis.

Applying the steady state treatment, the rate of disappearance of $S_2O_8^{2-}$, on the basis of above sequence of reactions, comes out to be

$$\frac{-d[S_2O_8^{2-}]}{dt} = k_1K[Ag^+][S_2O_8^{2-}] + k_4[R][S_2O_8^{2-}]$$

and since,

$$k_1K[Ag^+][S_2O_8^{2-}] = k_4[R][S_2O_8^{2-}]$$

hence,

$$\frac{-d[S_2O_8^{2-}]}{dt} = 2k_1K[Ag^+][S_2O_8^{2-}]$$

in conformity with the kinetic behaviour. However, in case of adipic acid, the monohydroxy adipic acid formed in stage 4 may only undergo stages 5 and 6 to yield mono-keto adipic acid (V), which decarboxylates to yield levulinic acid, as pointed out earlier.

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A Study on the Effect of Various Factors on the Slope, S_v, of Some Tetraalkylammonium Iodides in Some Nonaqueous Solvents

K. SINGH* and D. K. AGARWAL**

Chemistry Department, B. S. N. V. Degree College, Lucknow (U.P.)

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From the available data on apparent molal volume, φ_v, in various solvents at different concentrations for different tetraalkylammonium iodides φ_v vs. $\sqrt{C}$ curves are plotted and the values of slope, S_v, are obtained in the usual manner. A comparative study of the results in different solvents for a particular electrolyte and also for different R_4NI salts in a particular solvent indicates that the slope, S_v, decreases with the increase in the dielectric constant of the medium as well as with the increasing size of tetraalkylammonium ion with few exceptions; hydrogen bonding does not have any significant effect on the slope, S_v, values.

ONE of the fascinating subjects of study during the past few years has been the investigation of apparent molal volume of tetraalkylammonium and common salts in aqueous and nonaqueous solutions. The slope, S_v, of the φ_v vs. $\sqrt{C}$ curves has been found to be positive for some electrolytes while negative for others in different solvents. In aqueous solution positive slope of φ_v vs. $\sqrt{C}$ curves for common electrolytes as well as for tetraalkylammonium halides containing smaller R_4N^+ ions e.g., Me_4N^+ and Et_4N^+ and negative slope for the salts containing larger R_4N^+ ions at ordinary concentrations have been reported[1-4]. The negative slope in water has been explained by many workers[5-7] on the basis of enhancement of tetrahedral structure of water by hydrophobic R_4N^+-water interaction. This explanation seems to be not very convincing when the negative slopes have also been obtained for some R_4N X salts in some nonaqueous solvents like formamide, N-methylacetamide (NMA) and N-methylpropionamide (NMP)[8-10] etc. in which neither tetrahedral structure is present nor the hydrophobic interaction is expected.

Gopal and Siddiqi[8,9] suggested that the negative slope occurs if the volume of the solute ion is comparatively large as compared to the solvent molecule and if the interpenetration of the ions take place[11]. Gopal, Singh and Siddiqi[12] have also explained the negative slope obtained for some small and compact common ions in NMP and NMA on the basis that small solute ions are accommodated in the voids left in the packing of the solvent molecules.

Thus different explanations have been given for the positive and negative nature of the slope, S_v, of φ_v vs. $\sqrt{C}$ curves in case of different electrolytes in various types of the solvents, but none of them seem to be satisfactory for all types of the solutes and solvents. Since now sufficient φ_v data of R_4NI salts at different concentrations are available from which S_v values can be obtained by plotting φ_v vs. $\sqrt{C}$ in different solvents of varying dielectric constant, it seems desirable to tabulate them at a place and to see how the S_v values depend upon the physical properties of the solvent like dielectric constant, hydrogen bonding etc. and on the size of the ion. In the present communication, an attempt has been made to study the effect of dielectric constant, hydrogen bonding of the solvent and the varying sizes of the ion on the slope, S_v of the φ_v vs. $\sqrt{C}$ curves.

Results and Discussion

From the φ_v data obtained by our group[8,10,12], for tetraalkylammonium iodides in solvents of varying dielectric constant namely formamide, NMA, NMP, DMSO, PC and EC†, φ_v vs. $\sqrt{C}$ curves have been drawn and the slope, S_v, has been calculated in each case. The S_v values thus obtained have been listed in Tables 1 and 2. Table 1 consists of S_v values in nonhydrogen bonded solvents whereas table 2 contains that in hydrogen bonded solvents.

Effect of dielectric constant on slope, S_v

From the tables 1 and 2, it may be noted that a comparison of S_v values for a particular R_4NI salt in Dimethylsulfoxide (DMSO), Propylene carbonate (PC) and Ethylene carbonate (EC) on one hand and in Formamide, N-methylpropionamide (NMP) and N-methylacetamide (NMA) on the other hand indicate that S_v decreases with the increase in dielectric constant of the solvent provided that the solvents are of similar nature in some properties like dipole moment, hydrogen bonding etc.

* To whom all correspondence should be addressed.

** Chemistry Department, Lucknow University, Lucknow (U.P.).

† NMA = N-methylacetamide; NMP = N-methylpropionamide; DMSO = Dimethylsulfoxide,
PC = Propylene carbonate; EC = Ethylene-carbonate.

TABLE 1—S_v VALUES OF SOME R_4NI SALTS IN SOME NONHYDROGEN BONDED SOLVENTS AT 40°C

Solvent	S_v value for				
	Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI	Hep_4NI
Dimethylsulfoxide (DMSO) ($\epsilon_{25}° = 46.6$)	6.4	8.3	8.8	9.0	9.5
Propylene-carbonate (PC) ($\epsilon_{25}° = 64.72$)	4.7	4.5	4.2	4.0	3.6
Ethylene carbonate (EC) ($\epsilon_{25}° = 95.30$)	1.9	−1.5	−2.8	−4.0	−5.9

TABLE 2—S_v VALUES OF SOME R_4NI SALTS IN SOME HYDROGEN BONDED SOLVENTS AT 40°C

Solvent	S_v value for				
	Et_4NI	Pr_4NI	Bu_4NI	Pen_4NI	Hep_4NI
Formamide ($\epsilon_{25}° = 109.5$)	4.2	8.3	9.2	−6.6	−6'8
N-methylpropionamide (NMP) ($\epsilon_{25}° = 176.0$)	—	3.3	−1.2	−1.4	−1.6
N-methylacetamide (NMA) ($\epsilon_{25}° = 185$)	2.6	2.4	−7.0	−2.3	−2.0

The S_v values given in tables 1 and 2 are plotted against dielectric constant of the solvent and illustrative examples of the plots are demonstrated for Pr_4NI in figures 1 and 2, from which it is clear that a straight line is obtained in every case indicating direct dependence of slope, S_v, on dielectric constant of the solvent. This variation of S_v with dielectric constant may be explained on the basis that in case of solvents of medium and low dielectric constant, electrostatic interionic attraction will be appreciable and an ion is supposed to have strong influence on its neighbours. The extent of this interaction would depend upon concentration. This effect coupled with ion-solvent interaction although weak appears to be responsible for the positive value of S_v. While in the solvents of high dielectric constant (> 70), the electrolyte may assume to be completely ionised even at fairly high concentrations. The mutual penetration of the R_4N^+ ions and their penetration by I^- ions as well as entrapping[13,14] of the solvent molecules in the voids formed by the larger R_4N^+ ions seem to be in general responsible for the negative slope in the ϕ_v vs. $\sqrt{C}$ curves in these solvents of high dielectric constant.

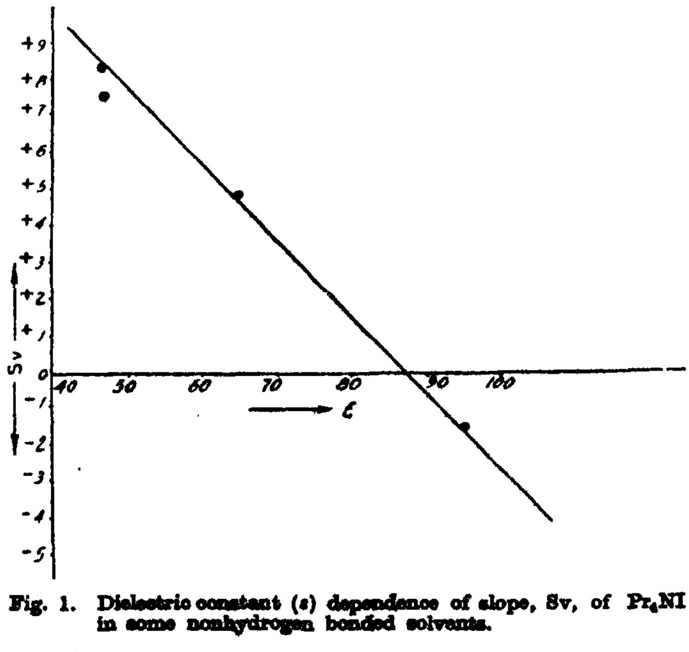


Fig. 1. Dielectric constant (ε) dependence of slope, Sv, of Pr_4NI in some nonhydrogen bonded solvents.

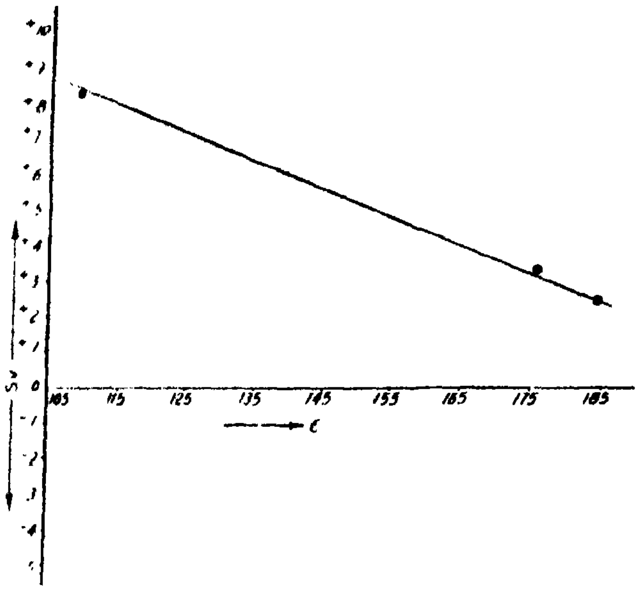


Fig. 2. Dielectric constant (ε) dependence of slope, Sv of Pr_4NI in some hydrogen bonded solvents.

Effect of hydrogen bonding of the solvent on S_v, values

From the tables 1 and 2, it may be noted that hydrogen bonding of the solvent has no significant effect on the S_v values. It is supported by the results of Padova *et al.*[15], who have reported positive slope of φ_v vs. $\sqrt{C}$ curves for all the tetraalkylammonium salts studied in methyl alcohol having sufficient hydrogen bonding. If hydrogen bonding has significant effect on S_v values then the slope of φ_v vs. $\sqrt{C}$ curves for larger tetraalkylammonium salts must be negative in methyl alcohol.

Effect of the size of the ion on S_v, values

From these studies, it is evident that in most of the cases the S_v values decreases with increasing size of the ion in a particular solvent. The slope becomes negative if the difference between the size of the ion and solvent molecule is too much. This is because of the fact that the chances of accommodation of solvent molecules in the voids formed by larger R_4N^+ ions are fairly good, if the size of the ions are larger than that of solvent molecules and vice versa.

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Polarographic Behaviour of 2-Mercaptoethanol at the D. M. E.

R. S. SAXENA and G. L. KHANDELWAL

Department of Chemistry, Malaviya Regional Engineering College, Jaipur

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The polarographic behaviour of 2-mercaptoethanol (OH CH_2CH_2SH) has been studied at ionic strength 0.1 *M* $NaClO_4$ in the *p*H range (1.42–11.20) at the d.m.e. The electrode process is reversible, diffusion controlled and involves one electron transfer process in the above *p*H-range. The effects of various supporting electrolytes viz., $NaClO_4$, Li_2SO_4, KCl, KNO_3 and $(C_2H_5)_4$ N Br; buffers viz., Britton-Robinson, Clark and Lube's, Michaelis-Borate, NH_3-NH_4 Cl, acetate and unbuffered media and different solvents such as methanol, ethanol, iso-butanol, acetonitrile, dimethylsulfoxide and dimethyl formamide have also been studied. The dissociation constant of the -SH group is found to be 9.50. Controlled potential electrolysis, interaction with mercuric chloride and mathematical analysis reveal the depolarisation of mercury with the formation of a Hg(I) complex, mercurous mercaptide (RSHg), which rapidly changes to more stable (2:1) mercuric complex $(RS)_2Hg$.

SAXENA *et al.*[1-3] have investigated the electrochemical behaviour of several mercapto compounds and their metal complexes which have found important application in biological, pharmaceutical and in resin industries. The present communication describes the polarographic behaviour of 2-mercaptoethanol in various supporting electrolytes viz., $NaClO_4$, Li_2SO_4, KCl, KNO_3 and $(C_2H_5)_4$N Br; buffers viz., Britton-Robinson, Clark and Lube's, Michaelis-Borate, acetate and unbuffered media and different solvents such as methanol, ethanol, iso-butanol, acetonitrile, DMF and DMSO for which there is no reference in the literature.

Experimental

2-Mercaptoethanol (referred to herein as RSH) and all other chemicals used were of anal-R (B.D.H.) quality. Freshly prepared solutions were used to avoid the effects of ageing and air-oxidation. A manual polarograph and Cambridge *p*H-meter were used for recording the polarograms and measuring *p*H, respectively. The capillary had the following characteristics in 0·1*M* $NaClO_4$, 0·002% Triton-X-100 (*p*H 4·80) at 0·10V vs S.C.E. with h_{eff} value of 50·75 cm, $m = 1{\cdot}24$ mg/sec, $t = 5{\cdot}00$ sec., $m^{2/3}t^{1/6} = 1{\cdot}594$ mg$^{2/3}$ $t^{-\frac{1}{2}}$. Polarograms were recorded in an inert atmosphere of nitrogen at (20±0·1°).

Results and Discussion

Effect of pH, *buffer constituents and ethanol concentration :*

Polarograms of 1·0 mM RSH in 0·1*M* $NaClO_4$ using 0·002% Triton-X-100 as maximum suppressor were recorded at different *p*H values in Clark and Lube's buffer. An anodic wave was obtained at all *p*H values (1·42–11·20) [Fig. 1]. The slopes of linear plots of $-E_{d.e}$ vs log $(i_d-i)/i$ showed that the electrode reaction was reversible involving one electron transfer process. The values of $E_{\frac{1}{2}}$ shift towards more negative potential with increase in *p*H [Table 2]. (The point of intersection of the

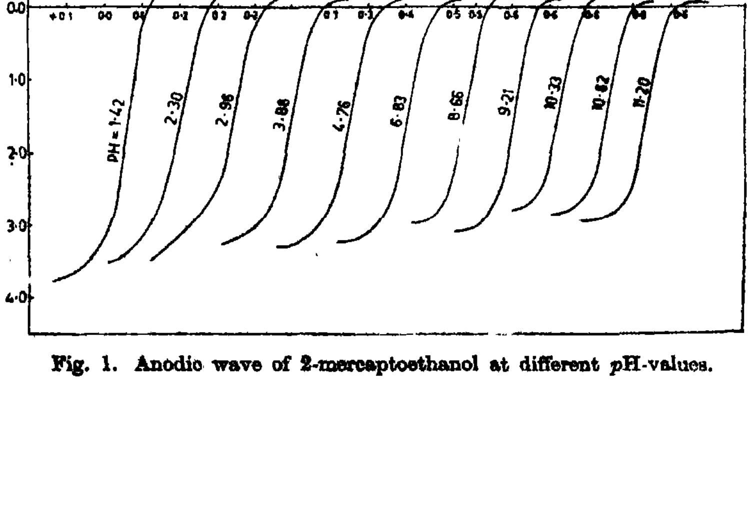


Fig. 1. Anodic wave of 2-mercaptoethanol at different *p*H-values.

plots of $E_{\frac{1}{2}}$ vs pH, corresponds to the dissociation constant (pK) of the sulphydryl group[3] and is found to be 9·50 (Table 2).

TABLE 1—EFFECT OF ETHANOL CONCENTRATION AT 20°C

Composition (water-alcohol) percentage	Diffusion current Constant (I)	Viscosity (Cp) (Incentipoise)
0.0	1.976	1.000
10	1.693	1.275
20	1.505	1.816
30	1.411	2.323
40	1.349	2.586
50	1.317	2.610
60	1.349	2.470

TABLE 2—EFFECT OF pH ON $E_{\frac{1}{2}}$

pH	$E_{\frac{1}{2}}$(V)
1.42	0.0600
2.30	0.1000
2.96	0.1400
3.88	1.1950
4.76	0.2490
6.83	0.3755
8.66	0.4825
9.21	0.5112
10.33	0.5341
10.62	0.5352
11.20	0.5370

The nature of the wave remains unchanged in various buffers such as Britton-Robinson, Clark and Lubo's, Michaelis-Borate, NH_3-NH_4Cl and acetate. In unbuffered media, an irreversible anodic wave was observed, this may be attributed to the change in pH due to the discharge of H^+ during the oxidation of RSH at the electrode surface[4].

i_d (total height of the wave i.e., diffusion current) was found to decrease with increase in ethanol concentration upto 50% beyond which it was found to increase. This may be ascribed to the change in viscosity of the solution with change in ratio of the ethanol and water[5] [Table 1].

Effect of ([*RSH*]*, Hg-pressure and temperature* : i_d changes linearly with [RSH] and mean value of I (diffusion current constant) was found to be 1·985. For 1·0 mM RSH $i_d/h^{\frac{1}{2}}_{eff}$ (0·434 μA cm^{-1}), temperature-coefficient of i_d 2·036% per degree were almost constant, indicating diffusion controlled nature of the wave.

Effects of various supporting electrolytes and solvents : i_d was measured at pH 4·80 using several supporting electrolytes and solvents. The values of diffusion current constant (I) were found to be in the following order :

$$(C_2H_5)_4NBr > KNO_3 > KCl > NaClO_4 \approx Li_2SO_4$$

and

acetonitrile > methanol > DMF > ethanol > DMSO > iso-butanol.

This may be due to variation in viscosity of solution[6] (I $\propto$ 1/viscosity).

Mechanism of the anodic reaction : Since the anodic wave produced by RSH is due to a reversible, diffusion controlled process, it is possible to get in indication of the mechanism of the anodic reaction. If the reaction is the oxidation of RSH to disulphide (RSSR) and the reaction is reversible,

$$2RSH \rightleftharpoons RSSR + 2H^+ + 2e^-, \quad \ldots (1)$$

then the potential at every point on the wave should be given by

$$E = \text{const.} + \frac{RT}{F}\ln[H^+]_0 + \frac{RT}{2F}\ln\frac{[RSSR]_0}{[RSH]^2_0} \quad \ldots (2)$$

which can be written

$$E = \text{const.} + \frac{RT}{F}\ln[H^+]_0 + \frac{RT}{2F}\ln\frac{i}{(i_d-i)^2} \quad \ldots (3)$$

At constant pH and at 20°,

$$E = \text{const.}' - \frac{0{\cdot}059}{2}\log\frac{(i_d-i)^2}{i}. \quad \ldots (4)$$

The other possible mechanism is the oxidation of RSH with intermediate formation of a free radical and the anodic dissolution of mercury, resulting in the formation of mercury-RSH complex,

$$RSH \rightleftharpoons R\dot{S} + H^+ + e^-, \quad \ldots (5)$$

$$2R\dot{S} \rightleftharpoons RSSR, \quad \ldots (6)$$

$$RSH + Hg \rightleftharpoons RSHg + H^+ + e^-. \quad \ldots (7)$$

Both (5) and (7) involve a one electron transfer process and the potential at any point on the wave is

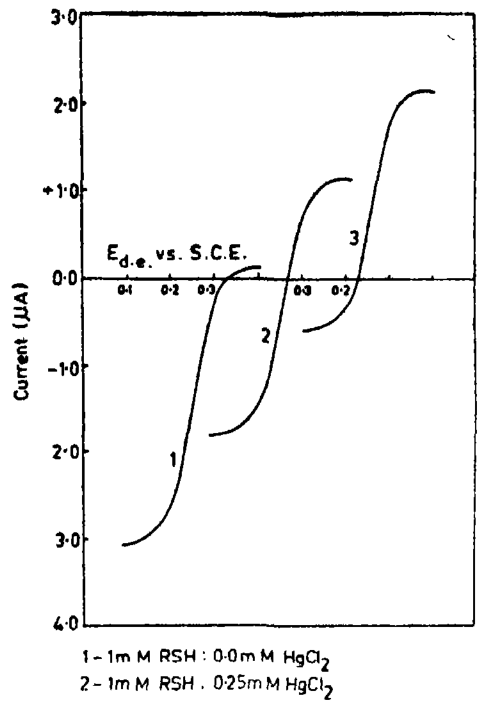
$$E = E_{\frac{1}{2}} - 0{\cdot}059\log\frac{i_d-i}{i}. \quad \ldots (8)$$

The plot of E vs $\log(i_d-i)/i$ gives a straight line with a slope (0·061±0·003), close to the theoretical[7] slope 0·059 (for one electron transfer) to allow the conclusion that (8) represents the electrode reaction. Furthermore it was found that the half-wave potentials were independent of RSH concentrations : this constancy of $E_{\frac{1}{2}}$ is characteristic of (8) but not of (4). The analysis indicates that the anodic reaction of RSH at the d.m.e. occurs either according to (5) and (6) or by the formation of the mercury-RSH compound, (7).

5·0 ml solution of RSH (1·0 mM), in 0·1M $NaClO_4$ at 0·10V (pH 4·80) was electrolysed in nitrogen atmosphere for six hours. Electrolysed solution was then polarographed under identical conditions : a cathodic wave obtained, which corresponded to a reversible[8] one electron reduction process. On passing H_2S through the electrolysed solution, a black turbidity was noted, showing the presence of soluble mercury in the solution. On the basis of

these observations, the reaction mechanism indicated by (4), (5) and (6) can be discarded. From the evidence we conclude that the product of the anodic reaction of RSH at the d.m.e. is a mercury compound of RSH.

With a view to obtaining more conclusive evidence, solutions containing (I), 1·0 mM RSH, (II) 1·0 mM RSH : 0·25 mM $HgCl_2$ (III), 1·0 mM RSH : 0·50 mM $HgCl_2$ were polarographed under identical conditions. Solution (III) yielded a well defined cathodic wave corresponding to one electron reduction having $E_{\frac{1}{2}}$ similar to that of anodic wave of solution (I). [Fig. 2,



3-1m M RSH : 0.50m M$HgCl_2$

Fig. 2. Comparative anodic-cathodic curves of RSH and mercury-RSH compounds.

curve-3 and 1], and solution (II) produced a composite wave, curve 2. These observations clearly indicate that the anodic reaction is solely due to the anodic dissolution of Hg forming its compound with RSH.

The curve for solution (II) showed large diffusion current at zero applied potential, but the same value of slope and $E_{\frac{1}{2}}$ as that given by solution (III), hence indicating the reduction of same compound mercurous mercaptide (RSHg) and the presence of free mercuric-ions[9]. These observations clearly reveal that the stable species of mercury and RSH is $(RS)_2Hg$ and the cathodic wave given by complex is due to the reduction of RSHg, an unstable compound. Moreover, the diffusion current constant of the complex was 3·39 as compared to 1·95 of RSH, indicating corresponding changes of $D^{\frac{1}{2}}$ values and consequently the size of reducing species. From diffusion current data[10], (taking Tl^{+1} as a reference substance) n has been determined $0{\cdot}89 \approx 1$ and hence the anodic wave of RSH represents one electron transfer process.

We may conclude that RSH is not oxidised to RSSR at the d.m.e. but it depolarizes the Hg with the formation of unstable RSHg. The reduction wave of $(RS)_2Hg$ corresponds to the reduction of a univalent cation. Hence, the reduction can be best represented by

$$RSH + Hg \rightleftharpoons RSHg + H^+ + e^- \quad \ldots (9)$$

$$2RSHg \rightleftharpoons (RS)_2Hg + Hg \quad \ldots (10)$$

Apparently (10) is very rapid, hence RSHg is reduced. Stricks and Kolthoff[11] have found a similar reaction with reduced glutathione.

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Studies on the Dissociation Constants of Indan Acids and their Hypoglycemic Activities

A. K. CHATTOPADHYAY and S. C. LAHIRI

Department of Chemistry, Kalyani University, Kalyani, Nadia, West Bengal

and

SAMIR CH. LAHIRI and JAYANTA K. GUPTA

Department of Pharmacy, Jadavpur University, Jadavpur, Calcutta-700032

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The dissociation constants of some indan acids, structurally related to hypoglycemic indole acids, were determined spectrophotometrically. Efforts have been made to correlate the dissociation constants with their hypoglycemic activities without much success. The observed activities of these carboxylic acids may be due to decrease in free acids in blood plasma. The results indicate that the highest activity is observed in compounds containing one methoxy substituent in the benzenoid part of the indan moiety.

THE biological properties of indane derivatives are wellknown. The indane nucleus has the molecular frame work which can fix the relative position of the biologically active moieties in a stereospecific manner making them pharmacologically active molecules[1]. The peculiar property prompted Lahiri and co-workers[2-4] to synthesize a number of indan acids and to utilise them as potent oral hypoglycemic agents. Since the potentialities of the drug molecules can be well-correlated by the various physico-chemical properties particularly by their dissociation constants, it was thought worthwhile to undertake the studies of the dissociation constants of the molecules by spectrophotometry. The results are described in this communication.

Experimental

The indan acids were prepared and purified in the same way as described elsewhere[5]. The solutions were prepared by direct weighing the acids and dissolving in water. KH_2PO_4 and Na_2HPO_4 (B.D.H.) were purified by crystallisation from water and dried. Perchloric acid and caustic soda were of E. Merck's reagent grade. The solutions were prepared using double distilled water.

For the determination of the dissociation constants of the acids, optical densities of various solutions of the acids were measured in the U.V. region. These were found to absorb strongly in this region. The reduced acids generally have absorption maxima around 265 nm whereas those of the keto acids lie around 250 nm and 285 nm (very weak). The positions of the absorption maxima (due to the ^1L_b transition of the benzene nucleus present in the compound) do not change appreciably with the changes in pH values. The changes in o.d. values in keto acids with changes in alkali concentrations (N/1000 to N/10) are not appreciable. The U.V. absorption curves of the acids in the molecular and ionic forms were obtained by measuring in excess acid ($HClO_4$) and in excess alkali (NaOH) solutions respectively. To have the accurate values of the dissociation constants, suitable wavelengths were chosen where the o.d. value of the two forms differ to the maximum extent but do not change appreciably with wavelength. First the approximate pK values of the acids were determined by suitable titration of the acids with alkali and measuring the pH of the solutions. The pHs at the half neutralization gave these values. For accurate determination of pH, the o.d. values of the acids ($\approx 3\times10^{-5}M$) in $KH_2PO_4+Na_2HPO_4$ buffers (with appropriate addition of KCl to keep the ionic strength at $0{\cdot}1M$) of pH values ranging between 6·0 to 7·4 and in N/10 $HClO_4$ and N/10 NaOH were taken at the analytical wavelengths. The blank solutions were of the same composition except the acids. The pHs of the buffers were measured with a cambridge bench type battery operated pH meter. All optical density measurements were taken with a Beckman DU2 spectrophotometer kept at 25°.

Results and Discussion

The thermodynamic dissociation constants K_T for the equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

is represented by

$$K_T = \frac{(H^+)(A^-)}{(HA)} \times f_{\pm}^2 \text{ (since HA is uncharged)}$$

or

$$pK_T = pH + \log\frac{C_{HA}}{C_{A^-}} - \log f_{\pm}$$

$$= pH + \log\frac{d_i - d}{d - d_M} - \log f_{\pm}.$$

where d_i = optical density of the ionic form
d_M = optical density of the molecular form
d = optical density at an intermediate pH.

The activity coefficient value at 0·1M was calculated using Davies[6] equation

$$-\log f_{\pm} = AZ_{+}Z_{-}\left[\frac{\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}} - 0{\cdot}2\mu\right].$$

The results are given in Table 1. The acids may be considered to arise from the replacement of H-atoms of formic and acetic acids by indan nucleus, a drastic reduction of pK-values is but expected. The keto-acids invariably have higher melting points than the corresponding reduced acids and as expected the keto acids are stronger than the reduced acids.

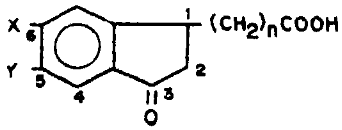
All these compounds show hypoglycemic activity to an appreciable extent. Though no correlation of the hypoglycemic activity with pK values can be made or no reason for hypoglycemic activity can be adduced, however, it may be said that hypoglycemic activity of all these carboxylic acids may be due to lowering of free fatty acid (FFA) level in blood plasma due to inhibited fatty acid synthesis. This is similar to the observations in case of salicylic acid, nicotinic acids etc. where it is amply demonstrated that a free carboxylic group or the facility with which the derivatives of pyrazole, isoxazoles etc. are converted to acids is necessary for hypoglycemic activity. Hypoglycemia is probably the result of increased glucose utilization when FFA becomes unavailable[7]. The structures of all these compounds are essentially of similar nature and it can be assumed that all these compounds act at the same site at the molecular level to lipid mobilization.

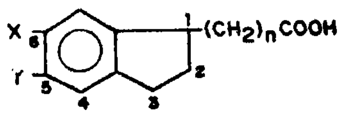
The pK values of the compounds lie between 6 to 7, a region of profound biological activity. It is not known that whether the dissociated molecule or undissociated molecule are responsible for effective drug action. The ionic form, if effective, would be present approximately 60–70 percent in the physiological pH region (pH of blood 7·4). It is admitted that the unionized molecules possess higher lipid solubility and pass most membrane barriers more readily than the ionized molecules. The prolonged action of some of these drugs (compared to tolbutamide) may be due to absorption of the non-ionized forms in the various lipids and slow release of these drugs when the ionized form are used up in course of time. It is to be noted that all these compounds showed peak hypoglycemic response between 6–12 hours and the activity was maintained upto 24 hrs or more.

It has been found that compounds with one methoxy compounds are more effective as hypoglycemic agents. We are not sure but probably hydroxylation of methoxy group (an effective process of drug metabolism) takes place during biotransformation which may be more effective as hypoglycemic agent.

One feature which deserve mention is that some of these compounds may be utilised as good buffers

TABLE 1

TYPE A 

TYPE B 

Sl. No.	Type	Compound	m.p	pK (+0.03) μ = 0.10	pK$_T$ (+0.03) (using Davies equation)	AV/Fall of Blood Sugar In normal intact rabbits	In alloxan diabetic rabbits
1.	A	X = Y = H, n = 0	120(H_2O)	6.23	6.34	12.5(±1.0)	
2.	B		55–56(H_2O)	6.50	6.61	17.4(±3.1)	
3.	A	X = OCH_3; Y = H, n = 0	187–188.5(H_2O)	6.30	6.41	20.0(±2.1)	28.2(±3.0)
4.	B		121–123	6.58	6.67	22.4(±1.4)	28.8(±3.0)
5.	A	X = Y = OCH_3, n = 0	190–191(H_2O)	6.38	6.49	15.7(±1.1)	
6.	B		114–115(C_6H_6)	6.66	6.77	14.1(±1.2)	
7.	A	X = Y = H, n = 1	153–154(H_2O)	6.37	6.48	9.8(±2.4)	
8.	B		55–56	6.60	6.71	16.3(±3.1)	
9.	A	X = OCH_3, Y = H, n = 1	151–153(alc+H_2O)	6.43	6.54	21.9(±2.1)	32.3(±4.3)
10.	B		97–98 (C_6H_6)	6.66	6.77	22.8(±1.3)	31.7(±3.4)
11.	A	X = Y = OCH_3, n = 1	175–177(H_2O)	6.48	6.59	17.2(±3.1)	
12.	B		159.5–161(50% alc)	6.74	6.85	19.2(±1.4)	25.4(±3.2)

A = Blood Sugar was determined by following the procedure of Jensen and Hagedorn[8]
B = Data on eight rabbits.

in the biological regions due to close proximity of pK values to the pH of the blood.

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Studies on Organic Sulfur Compounds as Emulsifying Agents

S. D. SHUKLA and KRANTI KUMAR

Chemistry Department, Lucknow University, Lucknow.

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Thiourea, thioacetamide, ammonium thiocyanate and phenothiazine which are listed as good fungicides in literature have been tried as emulsion stabilisers. The effect of addition of a few previously studied gums on the stability of emulsions stabilised by these organic sulphur compounds has also been studied applying the size frequency analysis of King and Mukerjee. It is concluded that single organic sulfur compounds are not capable of producing good and stable emulsions. Addition of Indian gums improves the stability coefficients and nature of the oil also plays an important role so far as the stability and the specific areas of the emulsions produced are concerned.

IN continuation with the previous work on arsenicals[15], copper compounds[16], D.D.T.[17] and Bordeaux mixtures[18] of different types the work has been further extended to the study of a few organic sulphur compounds.

Phenothiazine, thiodiphenylamine, introduced as an insecticide in 1935, may be considered one of the early members of the newer synthetic age. This compound has been reported as highly toxic to a number of insects, including mosquito larvae, aphids, codling moth and Mexican bean beetle[5,8,9]. Fungicidal value of phenothiazine has been noted by Goldsworthy and Green against apple scals, venturia inaequalis[14].

Thioacetamide (CH_3CSNH_2) is effective in reducing the decay in oranges caused by stem end rot and blue and green molds from about 40% to 2% or less[11]. It gives average control of the flesh fly larva, *Lucilia sericata*.

Thiocyanates include some of the earliest recognised effective insecticides used against aphids, mealy bugs and spider mites[6,7]. Wilcoxon and Hartzell published a series of papers[2,10] showing results from the use of various thiocyanates against aphids, and mealy bugs, *Pseudococcus* Sp; smaller European elm bark beetle, *Scolytus multistritus*, potato flea beetle, *Epitrix cucmeris* and spidermite, *Tetranychus telarius*.

Ammonium thiocyanate is used generally as a herbicide but with greator success on annuals than on perennials. The results are generally not as permanent as those from sodium arsenite and borex[4].

Thiourea (NH_2CSNH_2) is toxic to fresh fly larva, *Lucilia sericata*. It is also very effective against the house fly larva. A number of related compounds, including ethyl, methyl, propyl, butyl and amyl thiourea were effective against the flesh fly larva but at slightly higher concentrations than that of thiourea alone[1]. It is equally effective to thioacetamide against decay of oranges[11]. In the present work it is intended to study the above mentioned organic sulphur compounds as emulsion stabilisers which have been listed as good and representative insecticides and fungicides. The effect of addition of a few previously studied gums on the stability coefficients of these fungicides has also been studied.

Experimental

The gums were purified by the methods as described by Mukherjee and Shukla[12] in their earlier work on gums. The emulsions were prepared at 30° by King and Mukherjee's[3] method using fixed concentration of the sulphur compounds alone and then by adding fixed amounts of gums keeping the ratio of the oil (kerosene or olive) to water as 30 : 70 so that the emulsions produced were not very viscous and could be sprayed easily for practical purposes. The size frequency analysis was done immediately and on regular intervals of time on specific surfaces of these emulsions applying the theory of least squares as described by Mukherjee and Shukla[12,13].

Results and Discussion

A comparison of the data of size frequency analysis (table 1), in case of thioacetamide in combination with 0·1% Bel gum stabilized emulsions of kerosene and olive oils, reveals that although in emulsion no. 121 the finer particles of sizes 1μ-4μ were absent from the very beginning of preparation of emulsion and the percentage of 5μ particles was also low (89·18%), the dispersion varied from 89·18% (5μ) to 0·28% (25μ) on the first day, but the emulsion particles remained fine even after 2 months storage time as can be seen from the distribution of particles of various sizes.

On the other hand with the same system in case of olive oil emulsion some particles of sizes ranging between 1μ-4μ were present from the very beginning of preparation and particles of 5μ size were as high as 97·24%. A few parrticles of 2μ to 4μ sizes were present even after 6 weeks storage time. Rapid deterioration of the emulsion took place in this case

TABLE 1—PERCENTAGE DISTRIBUTION OF OIL DROPLETS OF DIFFERENT SIZES IN HOMOGENISED EMULSIONS.
(INDICES OVER THE EMULSION NO. DENOTE THE NUMBER OF WEEKS THAT HAVE ELAPSED)

Mean diameter (μ)	Emulsion no. → 121^0	121^{3/7}	121^1	121^2	121^3	121^4	121^6	121^8	134^0	134^{3/7}	134^1	134^2	134^3	134^4	134^6	134^8
1	—	—	—	—	—	—	—	—	0.61	—	—	—	—	—	—	—
2	—	—	—	—	—	—	—	—	0.99	1.81	1.75	1.57	1.13	1.25	1.30	—
3	—	—	—	—	—	—	—	—	0.68	1.45	1.64	1.69	1.58	1.19	1.00	—
4	—	—	—	—	—	—	—	—	0.36	0.45	0.66	0.75	0.56	0.99	0.90	—
5	89.18	85.55	76.86	75.90	72.50	—	72.23	70.77	97.24	94.93	93.45	91.42	90.65	73.87	50.50	34.74
10	8.11	9.81	14.35	15.00	15.30	—	16.62	15.92	0.12	0.94	1.44	3.15	3.61	9.48	19.00	27.51
15	1.53	2.18	3.15	3.20	3.67	—	3.75	4.77	—	0.27	0.57	0.76	1.13	6.98	14.00	18.34
20	0.90	1.52	2.31	2.40	2.65	—	3.22	3.66	—	0.15	0.33	0.48	0.90	4.49	9.00	13.02
25	0.28	0.94	1.85	1.90	2.04	—	2.14	3.18	—	—	0.13	0.19	0.45	1.25	3.30	3.32
30	—	—	0.83	0.90	1.02	—	1.18	1.27	—	—	—	—	—	0.50	1.20	2.57
35	—	—	0.65	0.70	0.82	—	0.86	0.95	—	—	—	—	—	—	—	—
40	—	—	—	—	—	—	—	0.48	—	—	—	—	—	—	—	—
Free Oil separation p.c.	(nil)	(0.25)	(0.5)	(0.5)	(0.5)	—	(1.0)	(1.5)	(nil)	(2.5)	(11.5)	(13.5)	(15.0)	(20.)	(24.0)	(28.0)
Agent	0.5% Thioacetamide+0.1% Bel Gum (Kerosene Oil Emulsion)								0.5% Thioacetamide+0.1% Bel Gum (Olive Oil Emulsion)							

as can be seen from the percentage of the particles of different sizes and this was due to rapid coarsening of the particles which took place with the ageing of the emulsion.

Stability : In table 2, the data on stability coefficients and specific areas have been collected. From this data it can be seen that :

In case of kerosene oil as internal phase no emulsions were possible with either of the three organic sulphur compounds.

However combination of Dhak gum with thioacetamide produced most stable emulsion with stability coefficient as 53·87. The least stable emulsion was obtained in case of ammonium thiocyanate with stability coefficient equal to 21·09.

Nature of Oil : With the above mentioned organi sulphur compounds as stabilisers the stability of a emulsion seems to vary considerably with the natur of oil. This variation is rather specific with differen agents and also with combinations of these agent with gums.

Except in case of ammonium thiocyanate, somewhat stable emulsions were produced with all othe single organic sulphur compounds.

In case of gum combinations with these agent (olive oil as internal phase) definite trends are obtained so far as the changes in stabilities and initial specifi area values are concerned. Stability coefficients i all the systems follow the same order : Dhak gum > Bel gum > original single substance > katira gum

TABLE 2—DATA FOR 30% KEROSENE OIL AND OLIVE OIL EMULSIONS

Emulsion no.	Gums	Kerosene Oil: Initial Specific Area ×10³ Calculated	Kerosene Oil: Initial Specific Area ×10³ Graphically determined	Kerosene Oil: Stability coefficient $K\times10^3$	Emulsion no.	Olive Oil: Initial Specific Area ×10³ Calculated	Olive Oil: Initial Specific Area ×10³ Graphically determined	Olive Oil: Stability coefficient $K\times10^3$
	0.5% Thiourea Stabilised Emulsions							
115.	Only thiourea	—	—	Broken	128	9.89	10.00	1.58
116.	+0.1% Dhak gum	14.77	11.22	30.83	129	6.03	5.75	32.61
117.	+0.1% Bel gum	7.95	6.31	39.84	130	13.42	11.75	11.35
118.	+0.1% Katira gum	7.56	7.24	0.89	131	—	—	Broken
	0.5% Thioacetamide stabilised Emulsions							
119.	Only thioacetamide	—	—	Broken	132	7.46	7.41	1.30
120.	+0.1% Dhak gum	14.78	10.47	53.87	133.	6.76	6.45	45.92
121.	+0.1% Bel gum	8.25	5.89	41.93	134.	13.81	11.48	11.90
122.	+0.1% Katira gum	—	—	Broken	135.	—	—	Broken
	0.5% Ammonium thiocyanate stabilised Emulsions							
123.	Only Ammonium thiocyanate	—	—	Broken	136.	—	—	Broken
124.	+0.1% Dhak gum	5.49	4.48	21.09	137.	2.97	2.95	84.53
125.	+0.1% Bel gum	15.18	15.14	126.20	138.	13.82	13.49	69.39
126.	+0.1% Katira Gum	—	—	Broken	139.	—	—	Broken
	0.5% Phenothiazine stabilised Emulsions							
127.	Only Phenotniazine	—	—	Broken	140.	—	—	Broken

Note.—Emulsions of Phenothiazine with combinations of gums were also broken immediately after preparation.

Ammonium thiocyanate emulsions in cases of different gum combinations showed a behaviour similar to those of thiourea in combinations with different gums as can be seen from the table 2.

Calculated initial interfacial area values and graphically determined initial interfacial area values showed a similar trend in case of different agents when used in combination with different gums.

Katira gum proved to be detrimental as emulsions were not possible with thioacetamide and ammonium thiocyanate. Very unstable emulsion was possible only in case of thiourea.

Practically determined initial specific area values an graphically determined ones also show a simila gradation. The order of decrease of these interfacia areas can be represented as follows :

Bel gum > sulphur compound alone > Dhak gun > Katira gum. Once more Katira gum proved to be detrimental in all the three cases of sulphu compounds.

In general kerosene oil emulsions were found to b finer in comparison to the olive oil emulsions as ca be seen from the size frequency analysis data as we as from the initial specific area values collected i table 2.

From the above discussion it can be concluded that single organic sulphur compounds are not capable of producing stable emulsions. Addition of Indian gums improves the stability coefficients probably due to greater adsorption of these gums at the interface and formation of viscous and tough film preventing the coalescence of the oil droplets.

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Corrosion of 63/37 Brass in Citric Acid Solution and Its Inhibition by Azole Type Compounds

N. K. PATEL, JUDAS FRANCO and I. S. PATEL*

Chemistry Department, Bhavan's R. A. College of Science, Khanpur, Ahmedabad-380001

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The inhibitory action of imidazole, benzimidazole, 2-mercaptobenzimidazole and 2-mercaptobenzothiazole towards corrosion of brass in 0.1 M citric acid was investigated. The inhibitory power of these compounds was found in the following order:

2-mercaptobenzothiazole > 2-mercaptobenzimidazole > benzimidazole > imidazole

Most of the compounds are able to form complexes with copper or/and zinc ions. The higher protection afforded by 2-mercaptobenzimidazole and 2-mercaptobenzothiazole may be due to formation of insoluble visible, adherent film on the copper surface. I.R. spectra of Cu-(MBT)$_2$ complex has been taken for the explanation of chelate formation.

1–2% citric acid is used as a cleaning agent for boiler at 45° in the presence of inhibitors[1]. Desai[2] reported the inhibitory action of gelatine towards corrosion of 63/37 brass in citric acid solution. Donaldson[3] reported the inhibitory action of benzotriazole towards corrosion of copper in citric acid. Citric acid is used as a automatic dish washers with detergent.

In the present investigation an attempt has been made to study the inhibitory action of some azoles towards corrosion of 63/37 brass in 0·2M citric acid solution.

Experimental

Brass (63/37) specimens were cold rolled and annealed at 550°. Rectangular specimens of size 6×3 cm (24 S.W.G.) were used. The composition of 63/37 brass was found as follows :

Experiments were carried out at 22±1°. 250 ml of 0·2M citric acid (BDH grade) was taken for the immersion of each specimen. The solution of citric acid was prepared in distilled water and solutions of inhibitors were prepared in ethanol. The procedures for preparation of specimen, testing and cleaning were adopted as described by Champion[4].

Results and Discussion

Results on weight loss are given in Table 1. Citric acid was found as a moderate corrosive agent for 63/37 brass.

* Chemistry Department, L. H. Science College, Mansa (N.G.).

TABLE 1

Reagents	Cu^{++}	Zn^{++}
	Colour of the precipitates	
Imidazole	Soluble dark blue coloured ppt	White insoluble ppt
Benzimidazole	No ppt	No ppt
2-mercaptobenzimidazole	Dull yellow	Light white ppt
2-mercaptobenzothiazole	Dark yellow	Light yellow amorphous

In the case of imidazole almost acceleration was observed. It afforded only 18% protection at its highest concentration i.e., 5·88×10^{-3} M. Benzimidazole afforded highest 33% protection at 3.42×10^{-3} M concentration. Its inhibitory action slightly increases with increase in concentration of the compound. 2-Mercaptobenzimidazole was found very effective inhibitor at its 2·67×10^{-3} M concentration. Its inhibitory action remarkably increases with increase in concentration of 2-mercaptobenzimidazole. In the case of 2-mercaptobenzothiazole 91% protection was noted at 2·39×10^{-4} M concentration. Its inhibitory action slightly improved with increase in concentration of the compound. It afforded 99% inhibition at its 2·39×10^{-3} M concentration. The inhibitory action of above stated compounds may be arranged as follows.

2-Mercaptobenzothiazole > 2-Mercaptobenzimidazole > Benzimidazole > Imidazole.

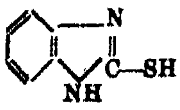
The compounds studied in the present investigation have the following structural formula.



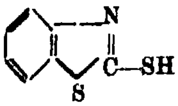
Imidazole



Benzimidazole



2-Mercaptobenzimidazole



2-Mercaptobenzothiazole

It is well known that thiazoles are excellent chelating agent for copper and zinc ions. Large volume of work has been done on azoles, particularly benzothiazole and 2-mercaptobenzothiazole as inhibitors for copper and its alloys in immersed and atomospheric conditions. The attachment of azoles with metal surface and the strength of metal inhibitor bond decides the effectiveness of the inhibitor. 2-MBT at its lowest concentration 1–10 ppm effectively retards the corrosion of copper in cooling tower system, and has hence been used nowadays[5–8]. Inder Singh[9] *et al.* reported the dissolution of mild steel in H_2SO_4 at 40° with and without 2-MBT. The corrosion rate, corrosion potential, anodic and cathodic polarization and H_2-absorption and permeability have been also studied.

In other series of experiment the inhibitors were tested as a chelating agents for copper and zinc ions which are the main constituents of 63/37 brass.

From the weight loss data it is clear that imidazole and benzimidazole are poor corrosion inhibitors while 2-mercaptobenzimidazole and 2-mercaptobenzothiasole effectively retard the rate of corrosion. The above table indicates the complex forming tendency of the latter two compounds with Cu^{++} and Zn^{+2} ions. From potentiometric analysis of the complex with Cu^{+2} and Zn^{+2} ions, it is found that solubility of copper complexes is less than that of zinc complex. The solubility product for Cu(2-MBT) is found to be 3.5×10^{-8}, while $Zn(2\text{-}MBT)_2$ complex is soluble to appreciable extent.

In aqueous solution 2-mercaptobenzothiazole ionizes as a weak acid. The ionic component forms insoluble salts with copper ions and conceivably the protective coating consists merely of the insoluble copper salt of 2-mercaptobenzothiazole. However, a more possible structure for the protective coating would take into account the fact that the 2-mercaptobenzothiazole possesses not only a ring sulphur, both capable of forming co-ordinate bonds with the metal ion.

The infra-red spectra of analytically prepared $Cu(2\text{-}MBT)_2$ complex indicates the covalent bonding between copper ion and 2-MBT which is through sulphur of the -SH group and a co-ordinate bond from sulphur which is in the thiazole ring. The I.R. spectra of $Cu(2\text{-}MBT)_2$ gives sharp band for stretching frequency of C–S at 1050 cm^{-1} and bending doublet for C–S at 740 cm^{-1} and 765 cm^{-1}. There is no SH band between 2600 and 2550 cm^{-1}.

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Ferric Salt as a Substitute for Conventional Coagulant in Municipal Water Treatment

M. ADHIKARI

Department of Applied Chemistry, Calcutta University

and

S. K. GUPTA and S. K. BANERJEE

Palta Laboratory, Palta Water Works, West Bengal

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Ferric sulphate is found to be a suitable and cheaper coagulant in Municipal Water treatment. The salt forms rapid, denser and easily settleable flocs particularly at low temperatures and thus possesses a number of additional advantages over other conventional coagulants.

A search for cheaper coagulant is gaining momentum for Municipal Water Treatment particularly in case where the source of water is surface one. A number of studies have been made with electrophoretic study using iron and aluminium salts in the domain of Public Health Engineering[1-3]. But a detailed study of ferric salt as a substitute for conventional coagulant in respect of utility and cost has not been made.

An attempt has been made to justify the suitability of ferric sulphate as a cheaper and more convenient coagulant for water treatment.

Experimental

River water samples (1 to 4′) were collected from the Ganges at the intake point of Palta Water Works, Barrackpore. All the physico-chemical analysis of water and the studies of coagulation characteristics were performed as usual. The average quality of river water under study was given elsewhere[4].

Commercial ferric sulphate used (as per AWWA B406-61T) was of the following specifications: (i) containing not less than 18% water soluble Fe^{+++} iron, (ii) not exceeding 3% soluble Fe^{++} iron, (iii) not exceeding 4% acidity as H_2SO_4, (iv) not exceeding 6% insoluble matter.

Basic alum used was as per ISI [16 to 17%, Al_2O_3, 0·5% Fe_2O_3, no As_2O_3] specification.

Results and Discussions

A comparative study with the aforesaid coagulants (vide Table 1) revealed the fact that quantitative requirement of ferric sulphate was lower than that of basic alum. It was possibly due to the fact that the concentration of Fe^{++} per unit mass of ferric sulphate was much higher in comparison to alum. Moreover, ferric sulphate produced rapid floc. Quicker settleable flocs formation due to higher bulkiness was an additional advantage.

The analysis of settled water after application of ferric sulphate showed a marked reduction in soluble silica content and total dissolved solid (TDS) percentage. On an average, 30% of TDS was diminished because of higher sorption on iron-clay floc particles. The *p*H zone of coagulation with ferric sulphate was substantially lower than the corresponding *p*H zone of coagulation with alum.

The working *p*H of ferric extends from *p*H 4 to 12 whereas alum is only effective within 6 to 8 *p*H. Thus above *p*H 8·0, the application of alum causes residual '*alumina carry over*' in the supply water whereas 'iron carry over' is very negligible owing to its low solubility as ferric hydroxide. An experimentation has shown that there is only 2 to 3% of iron retention in supply water for a raw water of turbidity 1000 p.p.m. when it is treated with 35 p.p.m. of ferric sulphate for optimal clarification. The favoured hydrolysis of ferric salt over alum is the cause for better coagulation of turbid water as shown by Miller[5]. The hydrolysed product is actually effective in reducing zeta potential of floc particles which lead to coagulation[2].

From another experimentation, it was observed that the consumption of ferric sulphate was 2·25 times lower than ferric chloride for optimal coagulation. It was due to participation of SO_4'' ion in secondary phase of coagulation[1]. $Fe\text{-(clay)}_x$ positively charged myceli did undergo neutralization[6].

With regard to working *p*H range the Ganges water at Palta point claims better suitability with ferric sulphate because *p*H level of raw water never falls below 8·0.

In 'monsoon period'[4], relative fineness of kaolinite clay particles (mechanically disintegrated) demands higher dosage of alum. The application of ferric sulphate has been extended to the coagulation of the Ganges water during monsoon period. For example, a typical river water sample of turbidity

TABLE 1—FOR OPTIMAL CLARIFICATION

Turbidity of River water	Alum reqd. in p.p.m.	Ferric sulphate reqd. (p.p.m.)	pH of alum treated water	pH of ferric sulphate treated water	Alkalinity of alum treated water (p.p.m.)	Alkalinity of ferric sulphate treated water (p.p.m.)	Salinity of alum treated water (p.p.m.)	Salinity of ferric sulphate treated water (p.p.m.)
817	36.40	25.80	7.70	7.60	80	76	12	13
984	35.70	23.20	7.60	7.50	72	65	25	25
1000	37.80	30.20	7.70	7.50	84	79	36	36
1083	42.00	33.60	7.70	7.50	88	80	12	12
1108	50.80	40.20	8.00	7.70	260	250	300†	298
1600	56.00	39.50	8.10	7.90	252	240	250†	240
1700	58.00	46.80	7.70	7.60	82	79	8	8

N.B. * Each level of turbidity is an average of 20 samples.
p.p.m. means mg litre.
† Higher salinity was before Farakka Discharge [owing to dilution with Farakka discharge salinity has gone down remarkably].

1200 p.p.m. required only 45·50 p.p.m. of ferric sulphate against the alum requirement 56·80 p.p.m. The clarity of settled water in the former case was also better.

Switching over to this newer coagulant, may invite some criticism from physiological standpoint. Analysis of settled water in ferric sulphate treatment revealed residual soluble iron below 0·5 p.p.m. i.e., within permissible limit of ICMR and WHO.

From the operational point of view, it is noteworthy that active matter concentration in ferric sulphate is much higher [20% Fe_2O_3 against 16 to 17% Al_2O_3 in alum]. Storage space requirement is very small i.e., 20 cft/ton. Sample of 95% purity also discharges very small amount of sludge in coagulant vat whereas basic alum leaves huge sludge deposit choking often the circulation pump line.

From the plant scale study it was shown that 2 to 2·5% of commercial ferric sulphate solution yields a pH within range of 3 to 3·5 that could be easily accommodated in the existing alum vat of the water works. To be overcautious against corrosion, one acid resistant bituminous paint would be sufficient on the cement concrete walls of alum vat.

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Novolak Based Adhesives for Metal-Metal Bonding

S. MEHRA, PADMA VASUDEVAN* and M. T. CHIPLONKAR

Chemistry Department, I.I.T., New Delhi

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Aluminium-Aluminium and steel-steel adhesive joints were made with novolak, cured with epichlorohydrin and starch under different conditions. The adhesive strength, both tensile and shear were determined and are discussed as a function of different parameters.

EPOXY resins are perhaps the best known metal-metal adhesives. Structural adhesives[1a] which are finding increasing importance in metal bonding are the two polymers adhesives that comprise of a thermosetting component along with a thermoplastic component. For example epoxy resins are used with nylon and phenolic resins with polyvinyl acetal, nitrile rubber resins or neoprene rubber. Pure phenolic resins also find a limited use, particularly where high hot strength is needed[1]. The type of phenolic resin used is an alkaline resol usually applied in ethanol or acetone solution. Accelerators such as sodium hydroxide or hexamine or mixtures of both are used. The adhesion to metal of unmodified phenolic resins can be increased by adding an epoxy resin and has been used in aircraft industry. Although generally it is the resol form which has been used in formulating adhesives it has been pointed out[1b] that in novolaks the phenolic groups are still free and by reaction with epichlorohydrin they can be converted into glycidyl polyethers which would be structurally similar to epoxy resins. Thus phenolic novolaks can form a cheaper substitute to bisphenol A. George and Rao[2] tested the use of epoxy novolak resin cured with aromatic diamines at an elevated temperature in wood, aluminium and wood to aluminium joints. Janis[3] discussed the properties of an epoxy novolak adhesive cured with pyromellitic dianhydride, and also of an epoxy novolak modified silicon-phenolic adheisive.

Thus, particularly in the light of the fact established by Narayanamoorthy and coworkers[4], at the Forest Research Institute in India that phenolic extracts can be obtained from tamarind seeds, tea wastes and species of trees growing in Asiatic mangrove forests and miscellaneous timber, we considered it of interest to experiment with novolak based resins. In the present work we have tested the use of starch as an additive to novolak and compared the adhesive properties with novolak cured with epichlorohydrin and hexa methylene tetramine under the same conditions.

Experimental

Phenol and formalin were taken in the ratio approximately 1 : 1 and were condensed with oxalic acid by refluxing at 80° for 3 hrs. The novolak was fluid and could be preserved for at least two or three weeks.

Cylindrical butt joints of aluminium-aluminium and steel-steel of various diameters were prepared and their area was determined both by geometry and by actual measurement of the area covered on a graph sheet. The aluminium surface was treated as follows : The specimen was immersed in a 1% solution of sodium hydroxide, and after washing with water was immersed in chromic acid solution, once again washed with water and dried. The steel surface was prepared as follows : The specimen was soaked in methyl ethyl ketone, immersed in oxalic acid solution, washed with water and dried.

A known weight of the novolak was mixed with calculated quantities of formaldehyde and a weighed amount of the curing agent (hexamethylene tetramine, epichlorohydrin, starch). The paste was evenly spread on the two faces of the joint. The ends were clamped together and cured at 70°/120° in an oven, and weighed. The total amount of resin in the joints was known quantitatively and the thickness was thus indirectly controlled. The ratio of the resin to the curing agent was 10 : 1. Also, as was done by Bryant[5] *et al.* an adhesive layer of known thickness was prepared by incorporating fine copper wires of diameter (1) 0·068 cm, and (2) 0·045 cm. The joints were cured for 24 hrs. After curing the tensil strengths of the joints were measured using a Hounsfield Tensiometer. Some samples were also boiled in water at 100° for 2 hrs, dried in the oven at 70° and tested.

For measuring the tensile-shear strengths, lap joints made up of rectangular aluminium and steel strips were used. The surface treatment and preparation of the joints were done as for the butt joints and after the test the exact area covered was found. The shear strength was also determined on a Hounsfield Tensiometer.

Results and Discussion

The tensile strngths of the butt joints cured with hexamethylene are shown in table 1, those cured with starch in table 2 and the ones cured with

* To whom all correspondence should be addressed.

epichlorohydrin in table 3. The shear strengths developed in a lap joint with these curing agents in the same order are shown in tables 4, 5, 6. In table 7 the tensile strengths developed in butt joints after incorporation of wire are given.

TABLE 1—TENSILE STRENGTH OF SPECIMENS CURED WITH HEXAMETHYLENE TETRAMINE

Type of Joints	Curing Temp. °C	Cylinder I : area 1.55 cm²		Cylinder II : area 6.1 cm²	
		Amount of Resin (gms)	Tension kg/cm²	Amount of Resin (gms)	Tension kg/cm²
1. Al-Al	70	0.2102	5.60	0.8166	5.30
		0.2152	5.16	0.8332	4.91
		0.2282	4.95		
2. Al-Al	120	0.2102	8.01	0.8432	7.50
		0.2108	8.32	0.8612	6.12
		0.2216	6.91		
3. Steel-Steel	70	0.2206	19.30	0.8156	20.50
		0.2212	18.70	0.8212	17.30
		0.2352	17.60		
4. Steel-Steel	120	0.2216	22.00	0.8328	23.20
		0.2218	21.60	0.8312	23.00

TABLE 4—TENSILE SHEAR OF SPECIMENS CURED WITH HEXAMETHYLENE TETRAMINE

Type of Joints	Curing Temp. °C	Amount of Resin (gms)	Tensile-Shear kg/cm²
Al-Al	70	0.5018	9.00
		0.5122	8.70
		0.5312	7.90
Al-Al	120	0.5132	10.10
		0.5256	9.50
		0.5532	9.32
Steel-Steel	70	0.5312	12.80
		0.5236	12.10
Steel-Steel	120	0.5202	14.50
		0.5226	13.92

To check for reproducibility several sets of readings have been taken with joints of different areas for a given set of constant curing conditions, regulated thickness and fixed resin curing agent ratio. Comparison with literature values[1a,7] is difficult as these are for much smaller weights of resin per unit area. Our data indicates that the tensile strength is highly sensitive to the weight of resin used, the general

TABLE 2—TENSILE STRENGTH OF SAMPLES CURED WITH STARCH

Type of Joints	Curing Temp. °C	Cylinder I : area 1.55 cm²		Cylinder II : area 6.1 cm²		Tension after boiling kg/cm²
		Amount of resin (gms)	Tension kg/cm²	Amount of resin (gms)	Tension kg/cm²	
1. Al-Al	70	0.2218	25.4	0.8302	26.5	—
		0.2326	24.5	0.8652	25.1	—
		0.2522	21.0			
2. Al-Al	120	0.2232	30.9	0.8102	32.9	20.0
		0.2358	29.7	0.8592	28.5	19.3
3. Steel-Steel	70	0.2232	59.2	0.8382	61.0	—
		0.2322	57.3	0.8812	58.3	—
4. Steel-Steel	120	0.2106	71.0	0.8352	73.2	54.6
		0.2252	68.6	0.9132	66.1	52.6

TABLE 3—TENSILE STRENGTH OF SPECIMENS CURED WITH EPICHLOROHYDRIN

Type of Joints	Curing Temp. °C	Cylinder I : area 1.55 cm²		Cylinder II : area 6.1 cm²		Tension after boiling kg/cm²
		Amount of resin (gms)	Tension kg/cm²	Amount of resin (gms)	Tension kg/cm²	
1. Al-Al	70	0.2056	36.1	0.8222	37.8	
		0.2122	33.5	0.8912	33.2	
		0.2282	29.0			
2. Al-Al	120	0.2106	71.0	0.8312	70.1	65.3
		0.2182	63.3	0.9232	61.0	62.7
		0.2204	62.3			
3. Steel-Steel	70	0.2134	59.8	0.8856	59.5	
		0.2136	57.6	0.9232	55.3	
		0.2202	52.3			
4. Steel-Steel	120	0.2252	121.2	0.8102	116.2	116.7
		0.2302	118.3	0.9152	109.3	112.6
		0.2528	111.3			

TABLE 5—TENSILE-SHEAR OF SPECIMENS CURED WITH STARCH

Type of Joints	Curing Temp. °C	Amount of Resin (gms)	Shear kg/cm²	Shear on boiling kg/cm²
Al-Al	70	0.5210	13.60	
		0.5286	13.06	
Al-Al	120	0.5018	15.20	11.3
		0.5312	14.50	9.8
		0.5322	14.10	
Steel-Steel	70	0.5032	21.60	
		0.5102	20.30	
		0.5236	19.60	
Steel-Steel	120	0.5212	23.40	20.5
		0.5364	22.40	19.6
		0.5432	21.10	

TABLE 6—TENSILE-SHEAR OF SPECIMENS CURED WITH EPICHLOROHYDRIN

Type of Joints	Curing Temp. °C	Amount of Resin (gms)	Shear kg/cm²	Shear after boiling kg/cm²
Al-Al	70	0.5232	11.30	
		0.5246	10.93	
		0.5306	10.52	
Al-Al	120	0.5102	25.20	21.0
		0.5252	24.50	20.2
		0.5396	23.50	
Steel-Steel	70	0.5202	33.60	30.6
		0.5216	32.80	29.6
		0.5356	32.10	

TABLE 7—EFFECT OF INCORPORATION OF WIRE ON TENSILE STRENGTH

Type of Joints	Curing Temp. °C and agent	Thickness cm	Tension kg/cm²
Al-Al	120 Starch	0.045	27.1
			26.5
		0.068	24.9
			23.2
Steel-Steel	120 Starch	0.045	62.5
			61.0
		0.068	56.9
			55.4
Al-Al	120 epichlorohydrin	0.045	64.3
			63.1
		0.068	60.5
			59.3
Steel-Steel	120 epichlorohydrin	0.045	105.5
			102.2
		0.068	99.9
			98.3

trend being an increase in strength with decrease of the weight. The plot of tensile strength versus weight of the resin is linear, but the experimental range over which the weight is varied is too small to give any conclusive results. It is seen that for a given curing agent the values for steel-steel joints are higher than for aluminium-aluminium joints. In all cases better strength was obtained on curing at 120° as compared to that at 70°. Although epichlorohydrin gave a stronger bond than starch cured at 120°, the strength with starch was as good as that for epichlorohydrin if the temperature of curing was 70°. The effect of thickness is also demonstrated by the values obtained for wire incorporated joints. However, unlike Bryant *et al*, we found that the incorporation of wire reduced the strength and hence comparison could not be made with values obtained without these inclusions.

The tests with the help of lap joints show similar trends except that the values are lower by nearly an order of mangnitude. Once again the strength is highly sensitive to thickness. On boiling with water there is no loss in the strength of joints cured with epichlorohydrin while the ones cured with starch lose some strength.

Conclusion

Novolaks can be used to give strong metal-metal adhesive bonds. Starch compares with epichlorohydrin in curing at low temperatures.

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Native Fixed NH_4^+ and the Fixation of Applied NH_4^+ in Some Soils of West Bengal

T. L. BHADURI, S. K. BANERJEE* and S. K. GUPTA

University College of Agriculture, Calcutta University, 35 Ballygunge Circular Road, Calcutta-19

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The soils of West Bengal contain an appreciable proportion of native fixed NH_4^+ and the values range from 114 to 354 ppm which contribute 59.7 to 93.6% of the mineral nitrogen of the soils. Significant correlation exists between native fixed ammonium and clay, C.E.C., total nitrogen and inorganic nitrogen of the soils. Fixation of added NH_4^+ increases with the increase of the concentration and with the increase of the pH of the soil fixation also increases but from pH 7 the fixation is practically constant. Amount of clay and C.E.C. of the soils are important factors which affect the fixation of added NH_4^+.

AVAILABLE evidence indicates that a considerable amount of soil nitrogen exists in the form of native fixed *ammonium*[1-3]. However, its proportion varies with the nature and characteristics of the soils. Per cent clay, nature of clay minerals, exchangeable potassium, amount of organic matter and cation exchange capacity[4-10] are the most important characteristics affecting the content of fixed ammonium in soils. Not much data on native fixed NH_4^+ and relative distribution of other forms of nitrogen are available for soils of West Bengal. The present work has, therefore, been undertaken to study the distribution of different forms of nitrogen in some soils of different agroclimatic regions of West Bengal. The present work also deals with the study on the factors affecting the fixation of added NH_4^+ in different soils.

Experimental

Soil samples were collected (0–15 cm) from 15 different regions of West Bengal. The soils were dried undershade, ground and passed through 80 mesh sieve. The relevant characteristics of the soils are given in table 1.

Native fixed NH_4^+ was determined by the method of Silva and Bremner[11]. Available nitrogen (soluble NH_4-N+exchangeable NH_4-N+NO_3-N) was estimated by the method as described by Jackson[12]. Total nitrogen was analysed by Kjeldahl method. The amount of organic nitrogen present was calculated by subtracting inorganic nitrogen (sum of the values of soluble NH_4^+, exchangeable NH_4^+, NO_3-N and native fixed NH_4^+) from total nitrogen.

TABLE 1—PHYSICOCHEMICAL CHARACTERISTICS OF THE SOILS

Soil	Predominant clay minerals	pH (1 : 2.5 ratio)	Clay (%)	Silt (%)	Sand (%)	Organic Carbon (%)	C.E.C. me/100 gm	Av. N. (ppm)	Total N (%)	Native fixed NH_4^+ (ppm)
Kalimpong	Illite	4.5	12.7	20.6	65.7	0.98	10.6	35.1	0.07	145
Mangpoo	,,	4.8	10.5	22.8	66.7	1.59	10.5	45.6	0.14	141
Alipurduar	,,	4.8	24.9	26.7	48.0	1.62	8.7	118.6	0.09	176
Purbasthali	,,	4.8	80.9	18.6	2.1	1.07	41.7	39.2	0.14	554
Jhargram	Kaolinite	5.3	22.5	21.0	56.7	0.30	8.6	10.2	0.04	149
Santiniketan	,,	5.9	11.5	7.0	75.0	0.30	3.4	30.2	0.03	114
Bishnupur	,,	6.0	14.5	12.0	73.5	0.38	5.9	35.0	0.05	145
Sriniketan	,,	6.2	17.6	3.3	79.1	0.29	7.9	24.6	0.03	161
Canning	Illite	6.4	42.1	43.2	14.7	0.81	18.6	35.0	0.09	212
Kalyani	,,	6.7	47.0	23.5	26.5	1.08	32.4	31.0	0.14	339
Baidyanathpur	,,	6.8	31.0	34.6	35.6	1.12	14.4	31.6	0.09	454
Baksha	,,	6.8	56.5	32.5	10.7	0.82	19.8	25.7	0.11	292
Ballapur	,,	6.9	38.3	37.3	23.9	0.75	16.7	40.6	0.08	395
Chinsurah	,,	7.1	54.2	28.1	17.7	0.96	33.5	26.0	0.09	227
Purulia	Kaolinite	7.3	22.2	18.2	59.6	0.30	7.2	24.6	0.03	162

All other characteristics of the soils were determined by the methods as described by Jackson (loc. cit.).

* Department of Soil Science and Ag-Chemistry, Bidhan Ch. Krishi Viswa Vidyalaya, Kalyani, Nadia.

Effect of different concentrations of added NH_4^+ on the fixation process

In this experiment 10 g of each soil in duplicate were taken in glass tubes and $(NH_4)_2SO_4$ solution @ 50, 100, 150 and 200 ppm of N were added and incubated in moist condition for 15 and 30 days at 25°. The amount of NH_4-N fixed in 15 and 30 days were estimated by Silva and Bremner method (loc.cit.).

Effect of pH on ammonium fixation

In this experiment soils of Santiniketan and Kalyani were used. The soils were treated separately with varying amounts of N/20 HCl and saturated $Ca(OH)_2$ solution so as to obtain soils of different *p*H's and incubated with $(NH_4)_2SO_4$ (100 ppm of N) in moist condition for 15 days at 25°. Control was run simultaneously. After 15 days, *p*H of the soils and amount of NH_4-N fixed were determined as usual.

Results and Discussion

The results presented in table 1 indicate that all the soils contain an appreciable amount of native fixed NH_4^+ and the values range from 114 to 554 ppm. Soils of Purbasthali, Baidyanathpur, Baliapur, Canning, Chinsurah and Kalyani, all of alluvial origin, contain higher amount of native fixed NH_4^+. This can be attributed to the presence of illitic types of clay minerals in these soils. On the otherhand, in red and lateritic soils (Purulia, Santiniketan, Sriniketan, Jhargram and Bishnupur), the native fixed NH_4^+ present is comparatively low which is attributed to the kaolinite type of clay minerals present in these soils.

But table 1 shows that the clay mineral is not the only factor for the differential amount of the native fixed NH_4^+ present in the soils. Purulia and Sriniketan soils contain higher amount of native fixed NH_4^+ than Mongpoo and Kalimpong soils though the first two are rich in kaolinite and the latter are rich in illite. Again, the soils of Purulia, Sriniketan, Santiniketan and Jhargram contain same amount of organic matter and the dominant clay mineral present in them is kaolinite but the amount of clay present in them is different and the quantity of the native fixed NH_4^+ varies. It is evident from the table 1 that higher the clay content the greater is the amount of native fixed NH_4^+ in these soils. The same sequence is observed in the soils of Purbasthali and Kalyani. These soils contain same amount of organic matter and the dominant clay mineral present is illite but they differ in clay content. Purbasthali soil contains higher amount of clay (80·9%) than Kalyani soil (47·0%) and the native fixed NH_4^+ in Purbasthali soil is high. In the soils of Canning and Baksha the same thing is observed. Therefore, it can be said that the amount of clay is an important factor which affects the content of native fixed NH_4^+ in soils. This is verified from the statistical analysis. Native fixed NH_4^+ gives a highly significant positive correlation ($r = 0{\cdot}7875^{**}$) with the clay content of the soils.

Cation exchange capacity is also another factor which affects the content of fixed NH_4^+ in soils. Correlation between native fixed NH_4^+ and c.E.c. of the soils is highly significant ($r = 0{\cdot}8698^{**}$).

Table 2 reveals that native fixed NH_4^+ contributes substantially to total nitrogen. This as a fraction of total nitrogen varies from 10·07 to 54·00%. Corresponding values reported by Raju and Mukherje[13] are 4·9 to 54·0% for some soils of West Bengal. Native fixed NH_4^+, on the otherhand, is accounted for most of the mineral nitrogen of the soils and varies from 59·7 to 93·6%. This is quite expected because the amount of available nitrogen present in the soils studied is very low. Table 2 also reveals that organic C/organic N values of all the

TABLE 2—DISTRIBUTION OF DIFFERENT FORMS OF NITROGEN

Soil	Total inorganic nitrogen (ppm)	Total organic nitrogen (ppm)	Native fixed NH_4^+ as a fraction of total nitrogen(%)	Native fixed NH_4^+ as a fraction of inorganic nitrogen(%)	Inorganic nitrogen as a fraction of total nitrogen(%)	Organic C / Organic N	Organic C / Total N
Kalimpong	180.1	519.9	20.70	80.5	25.7	18.9	14.0
Mongpoo	186.6	1213.4	10.07	75.5	13.3	13.2	11.3
Alipurduar	294.6	605.4	19.55	59.7	32.7	27.0	18.0
Purbasthali	593.2	806.8	39.57	93.4	42.3	13.4	7.6
Jhargram	159.2	240.8	37.25	93.6	39.8	15.5	7.7
Santiniketan	144.2	155.8	38.00	79.0	48.0	20.0	10.0
Bishnupur	180.0	320.0	29.00	80.5	36.0	12.7	7.6
Sriniketan	185.6	114.4	53.66	86.7	61.8	26.3	9.7
Canning	247.0	653.0	23.55	85.8	27.4	12.5	9.0
Kalyani	370.0	1030.0	24.21	91.6	26.4	10.8	7.7
Baidyanathpur	485.6	414.4	50.44	93.4	53.9	28.0	12.4
Baksha	317.7	782.3	26.54	91.9	28.8	10.5	7.5
Balipur	435.6	364.4	49.37	90.6	54.4	20.8	9.4
Chinsurah	253.0	647.0	25.22	89.7	28.1	14.7	10.7
Purulia	186.6	113.4	54.00	86.8	62.2	27.3	10.0

soils are higher than organic C/total N values. This indicates that inorganic nitrogen constitutes a considerable part of total N which is also supported from the data given in column 5 of the Table 2. The value varies from 13·3 to 62·2%.

Correlation coefficient values indicate that native fixed NH_4^+ is significantly correlated with inorganic nitrogen (r = ·9963**) as well as total nitrogen (r = 0·579*) whereas it does not bear any significant relationship with organic carbon (r = 0·3005).

The data on the effect of different concentrations of ammonium sulphate on the fixation of NH_4^+ are given in table 3. Table shows that in all the soils results but at high concentration the curve flattens out indicating that at low concentration NH_4^+ fixation is an adsorption phenomenon.

Table 3 also reveals that the fixation does not increase so much when the incubation period is increased from 15 to 30 days. This indicates that ammonium fixation is a rapid process and maximum fixation occurs within 15 days. The high rate observed at initial stage is probably due to the fact that the fixation proceeds from surface and edge to the interior of the particle.

The fixation of added NH_4^+ does not bear any definite analogy with the carbon content of the soils.

TABLE 3—FIXATION OF NH_4-N (PPM)* FROM THE ADDED $(NH_4)_2SO_4$

Soil	15 days' incubation				30 days' incubation			
	Treatments				Treatments			
	50 ppm	100 ppm	150 ppm	200 ppm	50 ppm	100 ppm	150 ppm	200 ppm
Kalimpong	20.0	29.8	42.6	58.5	22.8	32.5	45.9	61.6
Mongpoo	18.1	25.3	41.6	58.5	23.2	30.1	50.5	67.3
Alipurduar	26.5	41.2	60.3	76.2	30.1	44.8	67.1	79.8
Purbasthali	40.0	63.0	80.9	99.0	42.9	68.3	85.0	110.6
Jhargram	25.2	39.8	52.6	60.5	27.9	42.6	58.9	66.2
Santiniketan	15.7	23.4	30.8	40.0	20.2	28.2	32.8	45.8
Bishnupur	15.8	26.5	40.0	55.1	18.1	28.1	45.2	60.2
Sriniketan	19.6	38.2	50.6	61.2	26.0	40.2	56.8	65.1
Canning	28.6	42.0	66.7	88.2	33.8	45.8	68.4	91.7
Kalyani	34.1	51.2	64.8	96.0	38.9	53.6	70.1	104.1
Baidyanathpur	26.4	46.7	53.3	72.2	27.1	50.6	55.6	80.5
Baksha	33.2	54.5	68.5	91.2	36.6	59.8	73.1	95.6
Balipur	27.1	50.5	68.5	92.6	30.6	52.9	80.9	96.4
Chinsurah	32.2	50.2	71.3	95.6	36.0	58.4	75.2	102.8
Purulia	19.2	30.6	48.0	58.6	24.0	35.8	56.2	60.0
Mean values	25.4	41.1	56.0	78.1	29.2	45.5	61.4	79.4

* Average of duplicate determinations which were almost identical.

the amount fixed increases with the increase of the concentration of ammonium sulphate solution. Allison[14] explained this by suggesting the existence of equilibrium between three forms of NH_4-N :

$$\underset{\text{soluble}}{NH_4^+} \rightleftharpoons \underset{\text{exchangeable}}{NH_4^+} \rightleftharpoons \underset{\text{fixed}}{NH_4^+}$$

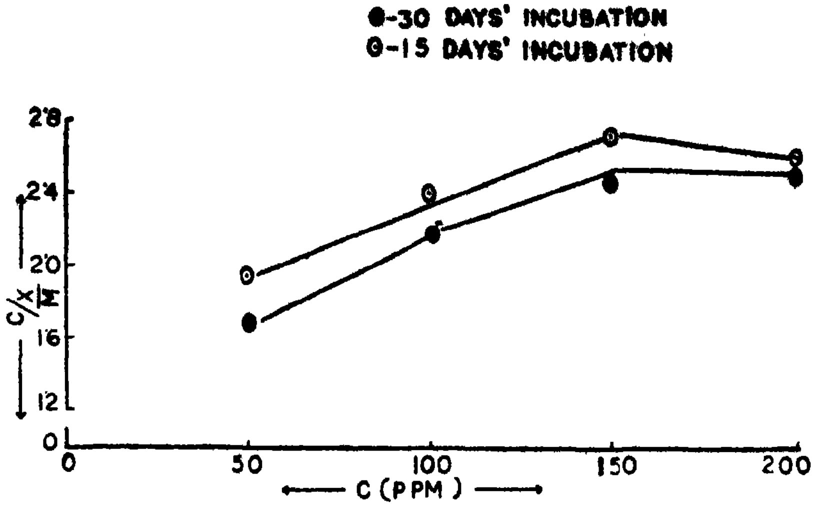
Since with the successive addition of NH_4-N the amount of available NH_4-N is always increased, the fixation will be increased upto a certain limit.

In order to see whether the ammonium fixation in soil follows the adsorption phenomenon, the mean values of the amount of NH_4^+ fixed in 15 and 30 days to all soils after addition of NH_4-N are calculated. Now $\frac{\text{equilibrium concentration}}{\text{mean values of } NH_4^+ \text{ fixed}}$ is plotted against equilibrium concentration $\left(C/\frac{x}{m} \text{ against } C\right)$. The figure shows that at lower concentration a straight line

It is found that some soils (Mongpoo and Alipurduar) containing higher amount of organic carbon fix a small quantity whereas the soils (Baksha and Kalyani) having comparatively lesser amount have the higher fixation capacity although all of them contain illite types of clay minerals. Mean value of the fixed NH_4^+ at four different concentrations of each soil bears a significant positive correlation with the clay content (r = 0·9368**) and c.e.c. (r = 0·8698**) of the soils. This indicates that fixation of added NH_4^+ also depends on the clay content and c.e.c. of the soils.

Table 4 shows that *p*H is also an important factor in NH_4^+ fixation. Acidification of soils markedly reduces the fixation capacity while with the increase of *p*H of the soils by the addition of $Ca(OH)_2$, the fixation capacity increases. This observation is in the line with that made by Karim and Malek[15] and Shoji and Mastumi[16].

Table 4 also shows that though the fixation increases with the increase in *p*H, the amount fixed is practically constant from *p*H near about 7.0. It is



PLOTTING OF $\frac{C}{X/M}$ AGAINST C

TABLE 4—EFFECT OF pH ON THE FIXATION OF ADDED NH_4^+

Kalyani Soil		Santiniketan Soil	
pH	Fixed NH_4-N (ppm)	pH	Fixed NH_4-N (ppm)
4.00	2.0	4.00	Trace
4.45	12.4	4.50	,,
4.80	20.4	4.90	4.0
5.95	31.0	5.20	15.6
6.70	50.2	5.50	23.8
6.80	51.2	5.80	26.8
7.00	51.5	6.65	31.1
7.30	52.0	6.80	32.2
7.50	53.0	7.30	33.1
—	—	7.40	34.5

also evident that pH level round about 6·7–7·0 is most favourable for the maximum fixation for both the soils having different clay contents and different clay minerals. Further studies are in progress in this regard for drawing definite conclusions.

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Studies on the Effect of Humic Acid in the Fixation of Added Ammonium in Some Soils of West Bengal

S. K. GUPTA, S. K. BANERJEE* and A. K. MUKHERJEE

University College of Agriculture, Calcutta University

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The effect of humic acid in the fixation of added NH_4^+ in six soils of West Bengal has been studied. The addition of humic acid decreased the fixation of NH^+_4 in the hydrogen peroxide treated soils. The fixation of NH^+_4 in the hydrogen peroxide untreated soils was greater than in the cases of hydrogen peroxide treated soils. But the addition of humic acid to the untreated soils greatly hundered the fixation.

IT has now been well established that ammonium ion applied as salts of strong acids to soils is rapidly incorporated into the organic and inorganic fractions of the soils and are unavailable to plants. The retention and fixation of ammonium ion have been studied by different workers[1-3]. They have shown that clay minerals of the 1 : 1 type or kaolin group fix little NH_4^+. In the 2 : 1 type of clay, minerals such as montmorillonite, vermiculite, illite vary in their ability to fix ammonium[4-6]. Ammonium can be fixed as a result of chemical interaction between soils and ammonium applied as aqueous ammonia, ammonia gas or ammonium salts[7-9]. The rate of fixation depends not only on the mineralogical status of the soils but also on the C/N ratio and other soil factors such as temperature, pH and chemical form of available nitrogen[10-13].

Since organic and inorganic fractions of the soils fix ammonium in different mechanisms, it was felt necessary to study the effect of one fraction to another on the fixation process. The present investigation, therefore, deals with the study on the fixation of added ammonium in presence and in absence of humic acid.

Experimental

Six soil samples (0–22 cm depth) collected from different agroclimatic regions of West Bengal were used in the experiment. The relevant characteristics of the soils are given in Table 1.

5 g portions of air dried, ground soil in duplicate were taken in glass tubes in two series. In one series 0·025 g and in the second 0·05 g of pure dialysed humic acid were added. 100 ppm nitrogen in the form of ammonium sulphate was then added to each tube and the soil was moistened with distilled water to ensure its 50 per cent moisture holding capacity. The tubes were stoppered and incubated for 15 and 30 days at room temperature and fixed ammonium was determined in duplicate by the method of Silva and Bremner[14].

TABLE 1—PHYSICOCHEMICAL CHARACTERISTICS OF THE SOILS

Soils	pH	Sp. conductance mmhos/cm	Organic carbon (%)	Total N (%)	C.E.C. me/100 gms	Native fixed NH_4^+ N ppm	Clay %	Silt %	Sand %	Dominant clay minerals
Sriniketan	6.15	0.071	0 290	0.029	7.9	161.0	17.0	10.0	71.1	Kaolinite
Bankura	5.80	0.170	0.114	0.010	8.6	149.8	18.5	21.6	60.7	Illite
North Bengal	4.80	0.412	1.618	0.098	18.7	176.4	26.7	24.9	48.4	,,
Canning	6.40	4.686	0.807	0.097	18.6	212.5	42.0	43.0	14.5	,,
Kalyani	6.65	0.284	1.083	0.136	32.8	339.8	47.0	23.5	26.5	,,
Chinsurah	7.10	0.362	0.955	0.096	33.5	327.2	54.2	28.1	17.7	,,

In another set of experiments, the soils were treated with 6 per cent hydrogen peroxide repeatedly to remove the native organic matter. The soils were then dried and ground. 5 g portions of these hydrogen peroxide treated soils were taken in glass

* Department of Soil Science and Ag-Chemistry, Bidhan Chandra Krishi Viswa Vidyalaya, Kalyani, Nadia.

tubes and same treatments as above were made and fixed ammonium was determined in each case in two different incubation periods.

Humic acid was extracted from Dehradun soil. The method of extraction and purification has been described earlier[15]. The physicochemical properties of the soils have been determined by standard conventional methods[16].

Results and Discussion

The amount of NH_4^+ fixed by organic matter free soils is given in Table 2. As these soils are free from organic matter, the amount of NH_4^+ fixed depends solely on the amount of clay and the nature of the clay minerals.

TABLE 2—FIXED NH_4-N AS PERCENTAGE OF THE ADDED NITROGEN IN HYDROGEN PEROXIDE TREATED AND UNTREATED SOILS

Soils	Treat-ments	Treated soils: Days of incubation 15 days	Treated soils: Days of incubation 30 days	Untreated soils: Days of incubation 15 days	Untreated soils: Days of incubation 30 days
Sriniketan	A	23.90	26.50	28.00	30.60
	B	18.60	20.80	23.20	25.40
	C	17.00	20.00	20.40	21.50
Bankura	A	20.70	24.50	26.30	29.70
	B	16.20	18.60	22.50	26.80
	C	14.80	17.00	22.00	25.20
North Bengal	A	34.40	38.00	39.50	40.80
	B	29.00	32.50	34.10	36.30
	C	26.50	30.60	32.60	33.80
Canning	A	37.60	41.20	42.00	45.80
	B	35.20	38.00	37.40	40.60
	C	31.30	32.60	37.00	40.00
Kalyani	A	43.20	47.80	50.20	53.60
	B	39.50	42.50	43.80	47.00
	C	38.00	41.00	41.60	45.80
Chinsurah	A	45.30	48.60	50.60	58.40
	B	40.80	42.80	41.80	44.50
	C	35.00	36.00	38.20	40.80

A = 100 ppm of N; B = A+0.5% humic acid; C = A+1.0% humic acid.

Sriniketan soil containing a large amount of sand (71·1%) and the clay minerals being predominantly kaolinite, fixed a small amount of added NH_4^+. With the increase of the incubation period fixation did not increase so much. The addition of humic acid decreased the fixation and with the increase of the incubation period there was a slight increase of fixation. The fixation further decreased when a greater amount of humic acid was added. The same sequence was followed in almost every case.

Table 2 shows that the soils of Kalyani, Chinsurah, Canning and North Bengal fixed greater amount of NH_4^+ than that of Sriniketan and Bankura soils because the former contains greater amount of clay fraction and the clay minerals present in them are mainly illite.

The amount of NH_4^+ fixed by H_2O_2 untreated soils is also furnished in Table 2. The table shows that in all the cases the amount of fixation is greater than in the case of H_2O_2 treated soil and the fixation increases with the time of incubation. The native soils contain mineral part and organic matter part. The organic matter contains both nonhumic and humic substances. The humic substances because of the presence in their molecules of the active functional groups react with the clay to form clay humus complex. Stable complexes are formed either when the humic anion penetrates the coordination shell of an iron and aluminium atom in the surface of the hydroxide and becomes incorporated into the surface hydroxyl layer or by hydrogen bonding[17]. In soils, clay-humus complex both stable and unstable forms are present. When NH_4^+ ion is added to the native soils, clay as well as the organic matter weakly bound to clay fix the added NH_4^+. But when humic acid is added in the system in pure form it quickly interacts with the clay fraction of the soil because of the presence in their structure the more active functional groups in comparison with the native soil organic matter and hinders the fixation of NH_4^+. It also may form a protective coating on the clay surface because of its large surface area and thereby blocks the fixation sites of the clay. The decrease in fixation can also be explained in another way. In the present case, Silva and Bremner's method was used to estimate the fixed ammonium. In this process KOBr was used to remove the organic matter part. If humic acid itself fixes the NH_4^+ in greater amount in comparison with the mineral part then the major portion of the fixed NH_4^+ will be removed by KOBr treatment. There are good evidences[18-20] regarding the fixation of NH_4^+ by humic substances. Therefore, this supposition cannot be ruled out. But this needs further verification and the work is in progress. Nevertheless, the decrease in fixation with the increase of the amount of humic acid strongly supports this view. However, if it is actually the case then it has some practial importance. Because, the NH_4^+ fixed by clay minerals is practically unavailable to the plants. But NH_4^+ fixed by organic fractions of the soil will be released after mineralisation and will be available to the plants.

In the case of H_2O_2 treated soils the situation slightly changes. Hydrogen peroxide reacts not only with the weakly bound but also with the strongly bound native organic matter and in the course of the reaction the H_2O_2 molecule penetrates the lattices of the clays and thereby rupture them. As a result the dimension of the space between the two plates most probably increases and therefore the added NH_4^+ does not fix so much and can be easily leached out by 1 N KCl solution.

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Relative Efficiency of Anions in Releasing Phosphate from Acid Soils

A. HAJRA and S. N. CHAKRAVARTI

Department of Chemistry, Vivekananda College, Calcutta-63, and
Department of Chemistry, Barasat Government College, Barasat, West Bengal

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Of the eight anions F′, Cl′, B′, I′, NO_3, S″, S_2O_3″ and SO_4″ studied, F′ is most effective in releasing phosphate from acid soils and SO_4″, the least. The order of efficiency of these anions in P-release is F″ > S″> $S_2O''_3$ > I′ ⩾ NO'_3 ⩾ Br′ ⩾ Cl′ ⩾ SO''_4.

NATIVE and applied phosphates in acid soils can be mobilized to some extent by the application of inorganic salt solutions. Cameron and Hurst[1] observed that neutral salts in general depress the solubility of $AlPO_4$ and KCl and $NaNO_3$ depress the solubility of iron phosphate. Hibbard[4] however observed that neutral salt solutions containing monovalent cation such as KCl, NH_4Cl, NH_4NO_3 and Na_2SO_4 extract about the same amount of soil phosphate as does distilled water, the effect of F′ in phosphate release from acid soils studied by various workers (Swenson *et al.*[8]; Turner and Rice[9]; Chang and Jackson[2]) Kar[6] observed that increase in calcium status gradually released soil phosphorus. The maximum release of phosphorus is noted with $Ca(OH)_2$ and is significantly higher than KOH and $Ca(NO_3)_2$. Gupta[3] observed that lime in combination with nitrogen as ammonium sulfate in general depressed the availability of P_2O_5 in the soil. Prabhakar *et al.*[7] observed that addition of both $(NH_4)_2SO_4$ and KNO_3 increased the available phosphorus content in red sandy loam soil (*p*H 6·7) but the effect of $(NH_4)_2SO_4$ was less as compared with KNO_3.

Experimental

In the present experiment three acid soils, two from West Bengal, viz., Kaksa (Burdwan), Mohammed Bazar (Birbhum) and one from Bhutan (Thimpoo) were used. The characterisation of the soil is described in Table 1.

2 gms of each of soil sample of Kaksa (K), Mohammed Bazar (M) and Thimpoo (T) was taken with 0·2 gm of the reagent in different stoppered bottles with 50 ml distilled water and kept for 3 months with occasional shaking. A few drops of toluene were added to check fungal growth. The reagents used were different salts of a particular cation i.e., Na^+ with different anions, in case of S″ alone CaS was used; *p*H being adjusted to 6·5 initially. After the desired period, the phosphate release was determined colorimetrically by the vanadomolybdate method (Jackson[5]).

The results are shown in Table 2.

Results and Discussion

The results indicate that anions are effective with a wide range from 8·0 to 87·7% in releasing phosphate from acid soils. Fluoride ion F′ is the most effective anion in such release and it releases phosphate about 86·5% from the soil, 87·7% from T-soil and 83·6% from M-soil. Next to F′ ion is sulfide ion, S″ this being probably due to the gradual precipitation of ferrous sulfide through the reactions :

$$\underset{\text{(acid)}}{CaS + SH^+} \rightarrow Ca^{++} + H_2S$$

$$2H_2S + FePO_4 \rightarrow 2FeS + H_3PO_4 + S$$

The release of phosphate by calcium sulfide is 29·7% for K-soil, 26·7% for T-soil and 27·3% for M-soil.

TABLE 1—SOME PARTICULARS OF THE SOILS

Locality	Latitude and Longitude of place	family	*p*H	Organic C %	C.E.C. me/100 gms	% of HCl soluble Fe_2O_3	% of HCl soluble Al_2O_3	% of HCl soluble P_2O_5
Kaksa (K)	23°28′ N+ 87°26′ E	Lateritic	4.80	0.43	5.25	4.45	5.05	0.084
Mohammed Bazar (M)	24°2′ N+ 87°2′ E	,,	6.15	0.52	10.35	3.05	4.35	0.076
Thimpoo (T)	27°30′ N+ 89°30′ E	Hilly forest	5.80	1.72	11.45	3.80	4.65	0.130

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TABLE 2—RELEASE OF PHOSPHATE BY DIFFERENT ANIONS

Soil sample	Treatment with	pH initial	pH adjusted	pH Final	Release of P in $g \times 10^{-6}$ per gm soil	% of P-release to total phosphorus content
I. K-soil	1. Water (control)	4.80	6.5	6.10	0.020	5.4
	2. NaF	6.20	6.5	5.65	0.320	86.5
	3. NaCl	4.15	6.5	6.10	0.040	10.8
	4. NaBr	4.25	6.5	6.15	0.043	11.6
	5. NaI	4.05	6.5	6.05	0.046	12.5
	6. $NaNO_3$	4.40	6.5	6.00	0.045	12.2
	7. Na_2SO_4	4.50	6.5	6.35	0.030	8.1
	8. $Na_2S_2O_3$	4.65	6.5	5.95	0.065	17.6
	9. CaS	7.15	6.5	5.85	0.110	29.7
II. T-soil	1. Water (control)	5.80	6.5	6.05	0.033	5.8
	2. NaF	6.15	6.5	5.30	0.500	87.7
	3. NaCl	5.30	6.5	5.90	0.057	10.0
	4. NaBr	5.50	6.5	5.85	0.058	10.2
	5. NaI	5.30	6.5	5.75	0.062	10.9
	6. $NaNO_3$	5.15	6.5	5.65	0.060	10.5
	7. Na_2SO_4	5.60	6.5	6.00	0.045	8.0
	8. $Na_2S_2O_3$	5.85	6.5	5.80	0.080	14.0
	9. CaS	7.10	6.5	5.70	0.150	26.7
III. M-soil	1. Water (control)	6.15	6.5	6.50	0.015	5.3
	2. NaF	6.35	6.5	5.50	0.280	83.6
	3. NaCl	5.50	6.5	6.00	0.031	9.7
	4. NaBr	5.70	6.5	5.95	0.033	10.0
	5. NaI	5.50	6.5	5.90	0.036	10.9
	6. $NaNO_3$	5.15	6.5	5.85	0.035	10.6
	7. Na_2SO_4	5.70	6.5	6.00	0.020	6.1
	8. $Na_2S_2O_3$	6.00	6.5	5.80	0.075	20.3
	9. CaS	7.30	6.5	5.70	0.090	27.3

The higher phosphate release by F′, obviously due to complex formation reaction and in the case of S″ is due to reduction of $FePO_4$ to FeS.

The slight higher release of phosphate by thiosulfate ion, S_2O_3'' than other anions e.g., Cl′, Br′, NO_3', I′ etc. is probably due to its weak reducing properties and complex formation reaction. The higher release of phosphorus by NO_3' than SO_4'' is probably due to its higher solubility and sorption properties.

The phosphate release property by different anions from K, T and M soils follow the order :

$$F' > S'' > S_2O_3'' > I' \geqslant NO_3' \geqslant Br' \geqslant Cl' > SO_4''.$$

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Mobilization of Phosphate in Relation to Ferrous-Ferric Equilibrium in Soil

S. K. BANERJEE, N. MUKHOPADHYAY and B. DAS

Department of Agricultural Chemistry & Soil Science, Bidhan Chandra Krishi Viswa Vidyalaya, Kalyani, West Bengal

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The mobilization of native and applied phosphate in relation to ferrous-ferric equilibrium in soil has been studied. Native phosphate has no significant and immediate role on the conversion of ferrous iron to ferric state. But the increase in phosphate activity enhances the degree and rate of oxidation of ferrous ions and as a result most of the applied phosphate are transported to the non-labile pool. The fixation of applied phosphate particularly in acid soils is very little effected by the exchangeable ferric iron. Possibly it is the free ferric oxide which is active in retention of phosphate.

WHEN a soluble phosphatic material is added to soil, it reacts with different components of soil and becomes relatively unavailable to plants. Among the various components, iron and aluminium and their free oxides are most important[1-6]. Dhar and Saxena[7] reported that the applied phosphate yielded highest amount of Fe-P in acid and neutral soils and Ca-P in alkaline soils; but Al-P did not follow this trend. Wild[8] noted the reduction in phosphate fixation caused by the removal of iron and aluminium oxides from soil colloids and the increase in phosphate fixation caused by addition of iron and aluminium compounds.

The present investigation has been carried out with a view to study the reversion of ferric iron to ferrous iron and vice-versa and its relation to available phosphate in soils.

Experimental

Seven different soil samples of West Bengal were used for the present investigation. Two acid terai soils from Alipurduar and Phansidewa belonging to the northern district, two lateritic soils and one red soil from Bankura, Jhargram (Midnapore) and Purulia respectively, one typical alluvial soil from Chakdah (Nadia) and one coastal alluvium from Kakdwip (24-Parganas) were obtained as usual (0–20 cm), air dried under shade, ground and sieved through a 0·2 mm sieve. The relevant characteristics of the soils are given in table 1.

50 g portions of each soil were taken in plastic containers and subjected to the following treatments. In one set phosphorus was added to the soil in the form of KH_2PO_4 at the rate of 100 ppm of P and in a second set ferrous iron in the form of freshly prepared $FeSO_4$ solution was added at the rate of 50 ppm of Fe while a third set contained both P and Fe^{2+} at the rates same as mentioned above. One set of soil samples was kept untreated which served as control. Distilled water was added to the samples in quantities corresponding to 50 per cent of the water holding capacity of the respective soils and the samples were incubated at room temperature for a maximum period of 6 weeks. Loss of moisture during incubation, as determined by difference in

TABLE 1—PHYSICOCHEMICAL CHARACTERISTICS OF THE SOILS

Soils	pH (1 : 2)	Organic Carbon (%)	Clay Content (%)	C.E.C. (me/100 g)	Water holding capacity (%)	Free Fe_2O_3 (%)	Available phosphorus (ppm)	Total phosphorus (ppm)	Dominant clay minerals
Alipurduar	5.4	1.060	28.0	8.9	50	0.87	14.8	500	Illite
Phansidewa	4.9	1.055	28.0	8.9	54	1.03	8.0	452	Illite
Bankura	5.6	0.600	20.0	10.2	35	1.82	3.2	276	Kaolinite
Jhargram	5.1	0.435	30.0	7.5	52	2.46	9.0	252	Kaolinite
Purulia	6.8	0.351	16.8	13.2	30	1.50	7.2	268	Kaolinite
Kakdwip	6.0	0.825	70.0	29.2	62	1.66	19.0	515	Illite
Chakdha	6.6	0.800	26.0	31.7	60	1.90	6.5	140	Illite

weights, was made up every day by adding requisite quantity of distilled water.

About 15 g of soil were drawn out with the help of a spoon-headed spatula at intervals of 7, 21 and 42 days, weighed and subjected to the determination of available phosphate and exchangeable ferrous and ferric iron respectively.

Available phosphate of the soil samples were extracted by Olsen's method and the phosphate content was determined by the colorimetric procedure as described by Jackson[9].

Exchangeable ferrous and ferric iron were determined colorimetrically by *o*-phenanthroline reagent as developed by Saywell[10] using normal ammonium acetate solution at *p*H 7·0 and *p*H 3·0 respectively as extractants.

A Spectronic-20 (Bausch and Lomb) spectrophotometer was used for all colorimetric measurements. The wavelengths of light beam employed were 608 nm and 490 nm for the determination of phosphorus and iron respectively.

All the reagents and chemicals used in the present investigation were of A.R quality.

Results and Discussion

The results of available phosphate determination are given in table 2. It appears from the data that while the original or untreated soils indicated a gradual increase in available phosphate status on prolonging the period of incubation the phosphate treated soils exhibited a rather decreasing trend. It is obvious that under the restricted soil moisture condition nearly 90 per cent of the applied soluble phosphate undergo fixation within 7 days of incubation. The minimum phosphate fixation (~ 80%) was observed in highly acidic Phansidewa soil and lateritic Jhargram soil. The fixation of phosphate in the soils under present study may be due to chemical precipitation mainly by ferric and aluminium ions or their free hydrous oxide micelle as well as due to ion exchange on the Kaolinite type of clay minerals.

The increase in available P status of the original soils on incubation may be ascribed to the gradual conversion of species like $FePO_4$ and $AlPO_4$ to the corresponding hydroxy or basic phosphates due to slight increase in soil *p*H by the influence of moisture. The rate of increase in fixation of applied phosphate indicates the kinetic of phosphate precipitation or phosphate exchange reaction by the appropriate constituents of the corresponding soils. Although the highly acidic Phansidewa soil exhibits an initial low degree of fixation, the subsequent increase in fixation on incubation was found to be maximum in this soil. The limited moisture status of the soil probably delayed the attainment of equilibrium point of phosphate fixation reactions involving active iron and aluminium present in it.

All the Fe^{2+} treated soils recorded a gradual decrease in available—P status on incubation. The Phansidewa soil showed a minimum while the lateritic Jhargram soil indicated maximum decrease in available phosphate. High acidity and high organic matter content of the former soil must have prevented the added ferrous iron from being oxidised and consequently precipitation of insoluble $FePO_4$ has been reduced. The low organic matter content, relatively higher Kaolinite dominant clay percentage and high free ferric oxide content may be responsible for quicker oxidation of Fe^{2+} ions followed by chemical precipitation of soluble-P already present in latter soil. Possibly, the Fe^{2+} ions might have also activated the reaction sites on free ferric oxide surfaces. Relatively higher phosphate activity as indicated by the initial high available-P status of this soil may also shift the equilibrium point of the following reaction towards right :

$$4Fe^{2+} + 4H_2PO_4^- + O_2 \rightarrow 4FePO_4 + 4H^+ + 2H_2O$$

The combined effect of phosphate and ferrous iron treatment is definitely less advantageous as is evident from the lower values of available-P for all

TABLE 2—AVAILABLE PHOSPHATE (PPM) IN THREE DIFFERENT INCUBATION PERIODS (on oven dry basis)

Soils	7 days				21 days				42 days			
	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} terated
Alipurduar	15.40	24.25	13.70	18.00	16.00	21.10	12.60	16.80	16.40	19.30	10.20	14.20
Phansidewa	8.85	29.80	8.00	15.40	9.70	21.10	7.00	12.60	9.80	17.20	6.65	10.80
Bankura	4.00	13.40	3.45	8.00	4.60	10.30	3.00	6.30	4.75	8.40	3.00	4.70
Jhargram	9.10	21.60	2.75	18.00	9.20	18.30	trace	11.90	9.40	15.20	trace	8.20
Purulia	7.75	21.15	6.95	13.10	8.00	17.70	8.00	10.90	8.20	14.50	5.10	8.40
Kakdwip	20.00	27.00	18.10	20.25	20.60	24.00	17.10	18.30	20.50	21.80	14.30	16.20
Chakdah	7.10	15.60	6.80	8.90	8.40	11.40	6.90	7.40	8.25	9.00	4.20	5.80

the soils in comparison to the values obtained for samples treated with phosphate alone. The available-P status of soils in such cases decreased steadily with duration of the incubation period. It is obvious that the increase in phosphate activity enhances the degree and rate of oxidation of Fe^{2+} ions and transport most of the applied phosphate to the non-labile pool.

The results of ferrous iron determination as shown in table 3 indicate marginally increasing trend for exchangeable Fe^{2+} status in all soils with the period of incubation. On phosphate treatment, an immediate lowering of exchangeable Fe^{2+} content was observed in all cases. No further significant change was observed on extending the period of incubation. Only the Phansidewa soil recorded an increase in exchangeable Fe^{2+} status. Obviously, the higher acidity of this soil encourages the Fe^{2+} ions to remain in solution. Since this soil initially contained a very small amount of Fe^{2+}, the immediate effect of increasing phosphate activity was to depress the Fe^{2+} activity almost to zero level due to decrease in formal potential of the Fe^{II}–Fe^{III} system.

incubation. Nearly 7–8% of added iron are transformed to the ferric state or immobilised in 7 days. Subsequent conversion was found to take place at a much slower rate obviously due to the fact that in presence of moisture soil samples were depleted of its oxygen content.

From table 4 it is evident that available ferric iron content of all the soils had undergone an initial reduction in amount. After 21 days of incubation there was virtually no further change in available Fe^{3+}. The phosphate treated soils behaved more or less in a similar manner. Added phosphate could only fix 6–10 per cent of the available Fe^{3+}. With increased period of incubation under the experimental condition, i.e., at moisture level corresponding to 50% of the water holding capacity of the soils concerned, phosphate ions appeared to be rather ineffective towards Fe^{3+} immobilisation. From the results it is clear that the fixation of applied phosphate in acid soils is very little effected by the exchangeable or available ferric iron. Possibly, it is the free ferric oxide or colloidal fraction which is more active in retention of phosphate through adsorption,

TABLE 3—FERROUS IRON (PPM) IN THREE INCUBATION PERIOD
(on oven dry basis)

Soils	7 days				21 days				42 days			
	Un-treated	P-treated	Fe++-treated	P+Fe++ treated	Un-treated	P-treated	Fe++-treated	P+Fe++ treated	Un-treated	P-treated	Fe++-treated	P+Fe++ treated
Alipurduar	9.0	7.2	15.6	11.2	9.6	7.0	16.2	10.2	10.4	7.0	18.4	9.8
Phansidewa	3.6	trace	11.8	7.2	4.7	2.0	13.4	5.8	5.3	5.0	16.0	5.2
Bankura	10.4	8.8	17.2	13.0	11.7	8.7	18.5	11.8	12.4	8.4	20.0	11.2
Jhargram	14.2	10.6	21.5	17.0	16.4	10.2	23.0	15.0	17.8	10.4	25.6	14.1
Purulia	11.2	9.0	19.3	13.8	12.5	9.0	20.4	14.0	13.8	8.9	22.8	12.8
Kakdwip	15.3	13.0	23.6	19.0	17.0	12.6	26.0	16.3	18.2	12.4	29.0	16.0
Chakdah	13.4	11.0	20.5	17.0	14.4	11.0	22.2	16.2	16.2	10.8	25.0	15.4

The effect of application of $FeSO_4$ to the soi was, in general, an increase in Fe^{2+} activity. But, while 50 ppm of soluble iron was added to each soil, after 7 days of incubation only an increase of about 8 ppm over control was observed. It is interesting to note that in respect of ferrous iron removal all the soils behave in a similar manner irrespective of their available–P status. It seems that native phosphate has no significant and immediate role on the conversion of ferrous iron to the ferric state. Restricted moisture level may be partly responsible for this. On extending the period of incubation, however, the influence of organic matter, clay percentage and their nature could be important. Decreased Fe^{2+} activity was noticed after 42 days of incubation in the soils which were richer in organic matter content.

On applying phosphate along with 50 ppm iron as Fe^{2+} in each soil, available ferrous ion status was found to decrease steadily with increasing period of occlusion or chemical precipitation as hydroxy phosphates.

Out of 50 ppm Fe^{2+} added, about 30 ppm had undergone rapid oxidation to increase the available Fe^{3+} status of all the soils. On extending the incubation period a tendency for decreasing available ferric iron was observed which might be due to fixation or by precipitation, hydrolysis or retention by clay-organic matter complex. The tendency was most pronounced for the Kakdwip soil which contianed as high as 70% clay and 0·825% organic carbon and also for the organic matter rich acid soil of Phansidewa which support the view that considerable amount of iron may be retained through the latter mechanism.

The addition of phosphate along with Fe^{2+} had an immediate depressing effect on total available ferric iron. On further incubation the reaction proceeded at a much slower but still considerable rate. Phosphate ions depress the redox potential

TABLE 4—EXCHANGEABLE FERRIC IRON (PPM) IN THREE INCUBATION PERIODS
(on oven dry basis)

Soils	7 days				21 days				42 days			
	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated
Alipurduar	76.0	70.0	106.0	96.0	74.0	67.0	104.0	92.0	74.0	67.0	104.0	92.0
Phansidewa	64.0	60.0	98.0	90.0	61.0	60.0	96.0	88.0	61.0	60.0	93.0	86.0
Bankura	300.0	288.0	328.0	306.0	295.0	284.0	323.0	296.0	295.0	284.0	320.0	298.0
Jhargram	200.0	189.0	220.0	212.0	195.0	185.0	224.0	204.0	195.0	186.0	222.0	203.0
Purulia	80.0	72.0	112.0	98.0	78.0	69.0	110.0	94.0	77.0	68.0	106.0	92.0
Kakdwip	40.0	36.0	70.0	64.0	37.0	35.0	68.0	60.0	37.0	35.0	66.0	60.0
Chakdah	160.0	152.0	190.0	178.0	157.0	153.0	184.0	174.0	156.0	152.0	184.0	170.0

TABLE 5—F_e^{3+}/F_e^{+2} RATIOS IN THREE INCUBATION PERIODS

Soils	7 days				21 days				42 days			
	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated	Un-treated	P-treated	Fe^{++}-treated	P+Fe^{++} treated
Alipurduar	8.4	9.7	6.8	8.5	7.7	9.6	6.4	9.0	7.1	9.6	5.5	9.4
Phansidewa	17.7	60.0	8.3	12.5	13.0	30.0	7.2	15.2	11.5	12.0	5.8	16.5
Bankura	28.8	32.7	10.07	23.5	25.3	32.6	17.4	25.1	23.8	33.8	16.0	26.6
Jhargram	14.1	17.8	19.7	12.5	11.9	17.1	9.7	13.6	10.9	17.9	8.7	14.4
Purulia	7.1	8.0	5.8	7.1	6.2	7.7	5.4	6.7	5.6	7.6	4.6	7.2
Kakdwip	2.6	2.8	2.96	3.4	2.2	2.8	2.6	3.7	2.0	2.8	2.3	3.7
Chakdah	11.9	13.8	9.3	10.5	10.9	13.9	8.3	10.7	9.6	14.07	7.3	11.0

of Fe^{3+}-Fe^{2+} system and enhance the rate of oxidation of Fe^{2+} which are subsequently precipitated as simple or basic ferric phosphates.

Changes of ferric to ferrous ratio, $[Fe^{3+}]/[Fe^{2+}]$ as evident from their available status are shown in table 5. It is found from the data that phosphate application has virtually no effect on the redox potential of the ferrous—ferric system as exist in the native soil. However, when fresh ferrous salt is added, applied phosphate enhances the rate of oxidation of the ferrous iron by affecting the redox potential of the system concerned.

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Notes

Aluminon as an indicator for EDTA Titration of Cupric Ions

B. B. PATEL, N. C. PATEL and B. N. SHAH

Department of Chemistry, Borsad Science and Law College, Borsad-388540, India

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ALUMINON (tri-ammonium aurine tricarboxylate) has been used as an indicator for EDTA titration of cupric ions. Titrations can be accurately carried out in the pH range 2·0–3·0.

The effect of variables such as concentrations, pH, temperature and foreign ions have been investigated.

Experimental

Copper sulphate solution : A stock solution of copper sulphate (0·1M) was prepared by dissolving 24·95 g copper sulphate in distilled water and making upto 1 liter.

EDTA solution : A stock solution of 0·01M Na-salt of EDTA was prepared by dissolving 3·723 g of EDTA in 1 liter of distilled water.

Indicator solution : 1·0% solution was prepared from pure sample of the reagent by dissolving the requisite amount in distilled water.

Metal solutions : To study the interference of various foreign ions in the estimation of Cu^{2+} with EDTA, the corresponding analaR quality of salts were taken and their 0·2M solutions prepared in distilled water.

Aluminon gives a pink colour with cupric ions. There is a sharp colour change on titration with EDTA from pink to light green as the end point approaches.

Effect of pH : When an aliquot of Cu^{2+} is titrated with EDTA, copper can be estimated accurately in the pH range 2·0–3·0 with the help of the indicators investigated.

Effect of Indicator concentration : Titrations were carried out with different concentrations of the indicator. It was found that an addition of 2 drops of 1·0% solution of the indicator gave satisfactory results.

Effect of Temperature : The titration could be satisfactorily carried out in the temperature range 10°–60°.

Effect of Foreign Ions : To investigate the effect of foreign ions, titrations of synthetic solutions were carried out at pH 2·0 maintaining the pH by acetate-HCl buffer. Preliminary investigations indicated that PO_4^{3-}, AsO_4^{3-}, S^{2-}, $Fr(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, CNS^-, CrO_4^{2-}, Fe^{3+}, Ni^{2+} Cr^{3+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Pb^{2+} and Al^{3+} interfere seriously. It was observed that at 1·3 mg concentration of copper, 10 times excess of Na^+, K^+, NH_4^+, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-} could be tolerated.

Suggested procedure : Take a 5·0 ml aliquot of solution containing cupric ions, adjust pH 2·0–3·0 using acetate-HCl buffer of pH 2·0, add 2 drops of 1·0% solution of indicator and titrate against 0·01M solution of EDTA with vigorous stirring to light green colour.

Standard Deviation : Five, 5·0 ml aliquots of 0.0·1M copper sulphate were analysed according to the suggested procedure. The standard deviation was 1·0%.

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Spectral Studies in Oxouranium(V) Compounds

MANGAL SINGH

Department of Chemistry, Guru Nanak Dev University, Amritsar

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COORDINATION complexes of U(V) with nitrogen and oxygen donor ligands have been characterised[1–4]. The complex, $(C_5H_5NH)_2UOCl_5$[5] has been shown to be an equimolar mixture of UCl_6^{2-} and $UO_2Cl_4^{2-}$ complexes[6]. The oxochloro complexes of U(V) of the formulae, M_2UOCl_5 [M = $(C_6H_5)_4As$[6], Cs[7], $(C_2H_5)_4N$[6–8]], $[(C_2H_5)_4N]_2$ $UOCl_5$. phthalazine[7], $[(C_2H_5)_4N]_2$ $UOCl_5$. bis (1,10-phenanthroline)[7] and $(C_5H_5NH)_2$ $UOCl_5.2{\cdot}5C_5H_5NHCl$[6] have been synthesised and characterised by spectral measurements. In the present paper the oxochloro complexes of U(V) of the type, $(BH)_2UOCl_5$ (B = pyridine, quinoline, isoquinoline, α-picoline and β-picoline) have been isolated from UCl_5 solution in $SOCl_2$ and characterised by IR, reflectance and ESR spectra.

Experimental

UCl_5 was prepared by refluxing UO_3 or UO_2Cl_2 with $SOCl_2$.[1–3] Pyridine, quinoline, isoquinoline, α-picoline and β-picoline (BDH AnalaR) were purified as already reported[3]. Compounds of U(V) are very

sensitive to moisture, therefore, filtration and drying have been carried out in dry atmosphere. Petroleum ether was dried by usual method and kept over sodium.

Pyridine, quinoline or isoquinoline (undried), cooled in an ice bath was added to an ice cooled solution of UCl_5 in $SOCl_2$ in a base/UCl_5 molar ratio of 2 : 1. Yellow solid in case of pyridine and reddish brown solids in the case of other bases, separated out on the addition of petroleum ether. These solids were repeatedly washed with dry petroleum ether and dried in vacuum. Picolines (undried) react vigorously with $SOCl_2$, therefore these bases were diluted with CCl_4 before addition to UCl_5 solution in $SOCl_2$. The analyses have been recorded in table 1.

Reflectance spectra of the pyridinium, quinolinium and isoquinolinium complexes show a sharp band at about 16665 cm^{-1}. This band is perhaps due to $\Gamma_7 \rightarrow \Gamma_8$ transition which has moved to a much higher energy in $(BH)_2UOCl_5$ compared to its position at 11,500 cm^{-1} in UCl_6^-. This is in agreement with the theoretical predictions[7]. However, some disproportionation during measurements is unavoidable and peaks also appear at 15625 cm^{-1} and 13158 cm^{-1} which correspond to U(IV).

ESR measurements on $(PYH)_2$ $UOCl_5$, $(QH)_2$ $UOCl_5$ and $(IQH)_2$ $UOCl_5$ (PY = pyridine, Q = quinoline and IQ = isoquinoline) produce strong and broad signal between 5900–5950 Gauss giving 'g' values of 1·12, 1·13 and 1·13 respectively. These 'g' values

TABLE 1—URANIUM (V) OXOCHLORO COMPLEXES

S.No.	Complex	Analytical Results					
		Found %			Required %		
		U	Cl	N	U	Cl	N
1.	$(C_5H_5NH)_2UOCl_5$	39.91	29.80	4.70	40.24	30.01	4.73
2.	$(C_9H_7NH)_2$*$UOCl_5$	34.15	25.47	3.99	34.41	25.67	4.05
3.	$(C_9H_7NH)_2$**$UOCl_5$	34.21	25.43	3.95	34.41	25.67	4.05
4.	$(C_6H_7NH)_2$***$UOCl_5$	38.31	28.43	4.50	38.42	28.65	4.52
5.	$(C_6H_7NH)_2$****$UOCl_5$	38.20	28.34	4.45	38.42	28.65	4.52

* = quinolinium, ** = isoquinolinium, *** = α-picolinium, **** = β-picolinium.

Uranium was estimated gravimetrically as well as volumetrically[2]. Chlorine was estimated volumetrically by Volhard's method. Nitrogen was determined in the microanalytical laboratory.

IR, reflectance and ESR spectra were recorded on spectrophotometers already described[2].

Results and Discussion

The elemental analyses of the oxochloro complexes correspond to $(BH)_2UOCl_5$. These complexes are stable under anhydrous conditions and disproportionate into U(IV) and U(VI) in moisture. On thermal decomposition these complexes give U_3O_8 at about 600°.

The IR spectra of the complexes in nujol mulls have been recorded. A strong band at 2845, 2835 cm^{-1} and a broad band between 2925–2825 and 2925–2850 cm^{-1} conforms to $BH^{+\bullet}$ (B = pyridine, isoquinoline, quinoline and β-picoline respectively). A very strong band in all these oxochloro complexes at 910 cm^{-1} may be assigned to the U = O stretching frequency[6,7].

are in good agreement with the calculated and experimental values of 1·04[7] and 1·09[7,8] for $[(C_2H_5)_4N]_2$ $UOCl_5$ indicating similar arrangement around Uranium(V) in these complexes.

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Adducts of Some Unidentate Ligands with Tetrathiocyanato Zinc(II) Complexes

S. GURU*

P. G. Department of Chemistry, Ravenshaw College, Cuttack-3

and

V. S. R. GUPTA & A. PANDA

G. M. College, Sambalpur

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TETRAHALO zinc(II) complexes and their reactions with different nitrogen ligands and a sulphur ligand have been reported[1-5] earlier. Ligands containing nitrogen as donor atom are bonded strongly to zinc(II) ion whereas sulphur coordination is not very strong. Penta-coordination in zinc(II) complexes was reported[6] by us in an earlier communication. We report here some mixed ligand complexes obtained by reacting tetrathiocyanato zinc(II) compound with pyridine, 4-methyl pyridine, quinoline, iso-quinoline and thiourea. The compositions of the compounds actually isolated with some of their physico-chemical properties and analytical data are incorporated in Table 1.

TABLE 1—M.P., ANALYSIS AND CONDUCTANCE OF TETRATHIOCYANATO ZINC (II) COMPLEXES

Complexes	Colour and form	M.P.°C	% of Zinc		% of SCN		Λ in mhos cm² in acetone
			Found	Calcd.	Found	Calcd.	
$[Me_4N]_2[Zn(SCN)_4]$	White and micro crystalline	165	14.50	14.60	51.60	52.20	249
$[Me_4N]_2[Zn(SCN)_4PY_2]$	Light yellow crystalline	118	10.50	10.77	38.00	38.47	220
$[Me_4N]_2[Zn(SCN)_4Q]$	-do-	160	11.00	11.30	40.90	40.41	230
$[Me_4N]_2[Zn(SCN)_4(IQ)_2]$	White crystalline	109	9.10	9.24	33.80	33.00	225
$[Me_4N]_2[Zn(SCN)_4(\gamma\text{-pic})_2]$	Light yellowish crystalline	117	10.14	10.31	37.00	36.76	220
$[Me_4N]_2[Zn(SCN)_4tu]$	White crystalline	139	12.10	12.47	45 00	44.51	230

Experimental

All the chemicals used are of AnalaR grade. The purity of the isolated compounds was established by estimating the metal and thiocyanate following standard methods.

To the suspension of the tetramethyl ammonium tetrathiocyanato zinc(II) complex in ethanol, the ligand was added in 1 : 2 ratio. The reaction mixture was refluxed for 5 hrs, in the case of pyridine, 1 hr in case of 4-methyl pyridine and 2 hrs when the ligands were quinoline, iso-quinoline and thiourea. The resulting solution on cooling deposited crystalline complexes. They were filtered under suction, washed with ethanol followed by ether and dried in vacuo.

All the complexes are fairly soluble in acetone. The conductance measurements were carried out at 27° with 10^3M solutions in acetone medium using a Toshnical Conductivity Bridge and a dip type cell. The infrared absorption spectra of the ligands and the complexes were recorded in the region 4000–650 cm^{-1} in Nujol mulls using a Unicam SP 200 double beam spectrophotometer.

Results and Discussion

When the tetrathiocyanato zinc(II) compound was reacted with ligands containing nitrogen or sulphur-donor atoms, reaction did take place forming entirely new compounds whose form, melting point and other characteristics were completely different from those of the starting materials. Analyses of the complexes for metal and thiocyanate reveal the formation of anionic complexes. In acetone medium, the Λ_M values for 2 : 1 electrolytes are usually round about 240 mhos and hence the values for Λ_M recorded in Table 1, show that these complexes are all 2 : 1 electrolytes and this observation is in confirmity with their formulae.

Infrared Spectra :

The infrared frequencies of the thiocyanate groups in the complexes are listed in Table 2. Very sharp bonds were observed near 2050 cm^{-1} and sharp bands near 700 cm^{-1} in all the cases. Terminal and bridging thiocyanato groups have been distinguished[7]

TABLE 2—INFRARED FREQUENCIES OF THE TETRATHIOCYANATO ZN(II) COMPLEXES

(Values in cm^{-1})

Complex	ν(C-N)	ν(C-S)
$[Me_4N]_2[Zn(SCN)_4]$	2050	700
$[Me_4N]_2[Zn(SCN)_4PY_2]$	2060	718
$[Me_4N]_2[Zn(SCN)_4Q]$	2070	700
$[Me_4N]_2[Zn(SCN)_4IQ_2]$	2060	710
$[Me_4N]_2[Zn(SCN)_4tu]$	2080	710
$([Me_4N]_2[Zn(SCN)_4(\gamma\text{-Pic})_2]$	2070	720

earlier and accordingly there are only terminal groups in the compounds reported here. Turco[8] has distinguished between frequencies for M-SCN and M-NCS compound. The compounds reported here seem to possess M-NCS groups.

Further infrared spectra of the complexes show strong absorption bands of both the tetramethyl ammonium ion (745 cm^{-1} and 970 cm^{-1}) and the ligands. The shifting of ligand absorption bands as seen in the infrared spectra of the complexes are indicative of definite metal ligand bonding.

The complexes having the formula $[Me_4N]_2[Zn(SCN)_4L_2]$ where L is pyridine, 4-methyl pyridine and isoquinoline, seem to have hexa coordination, whereas the complexes $[Me_4N]_2[Zn(SCN)_4L]$ where L = quinoline and thiourea are possibly penta coordinated. The exact coordination number can be established only by X-ray studies.

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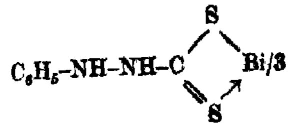
Determination of Bismuth with Ammonium Phenyldithiocarbazate as a Gravimetric Reagent

Y. K. Kakkar & K. S. Boparai

School of Studies in Chemistry, Vikram University, Ujjain-456010

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MUSIL and Hass[1] studied the analytical characteristics of ammonium phenyldithiocarbazate. The reagent has proved useful for many of the sulphide forming cations. The present report records the results of the gravimetric determination of bismuth(III) which is precipitated quantitatively in the pH range 0·8 to 6·3. Many a organic precipitant[2-4] has been suggested for the gravimetric determination of bismuth. The use of the present reagent, however, is advantageous in certain respects. The reagent is very easily prepared, readily soluble in water and stable in the solid form. The bismuth complex is of definite composition and hence directly weighable. The complex, though unstable in the hot acid medium, is sufficiently granular and easily filterable at room temperature. In the presence of EDTA the procedure is appreciably selective for the determination of bismuth. The following structure of the bismuth complex formed is suggested from its analytical data.



Experimental

Bismuth(III) Solution: Bismuth Nitrate pentahydrate (3·5262 g) of B.D.H. quality was dissolved in 1 litre of distilled water and acidified with nitric acid. Bismuth was determined as pyrogallate[5]. An aliquot was then suitably diluted to prepare a 0·1% solution of the metal.

Reagent Solution: Aqueous solution of the reagent (1·0%) prepared freshly was used for the determination.

Determination of Bismuth: Twenty five ml. of the bismuth solution was taken in a 500 ml beaker and diluted to about 130 ml. Ammonium Nitrate (2·5 g) and ten ml. of sodium potassium tartrate (10%) were added; the pH of the solution was adjusted between 5 to 6 by the addition of sodium acetate solution (10%). The reagent solution was then introduced dropwise with continuous stirring of the contents of the beaker. The yellow precipitate thus obtained was further stirred for about 10 mins. and then allowed to stand for half an hour. It was then filtered through a sintered glass crucible (G3), washed with water, and dried to a constant weight at 100° in about one and a quarter hours. The results are recorded in Table 1. The weight of the precipitate multiplied by 0·2754 gives the weight of bismuth.

Table 1—Determination of Bismuth(III) in presence of Diverse Ions
(25 mg of Bismuth taken for each determination)

Diverse ion	Added as	Amount added mg.	Bi Complex mg.	Bi found mg.	Error mg.
—	...	—	90.9	25.03	+0.03
—	—	—	90.7	24.98	−0.02
—	—	—	90.7	24.98	−0.02
—	—	—	90.8	25.00	0.00
K(I)	Nitrate	100	91.4	25.17	+0.17
Ca(II)	Chloride	100	91.8	25.27	+0.27
Ba(II)	Nitrate	100	90.5	24.92	−0.08
Sr(II)	Nitrate	100	90.9	25.03	+0.03
Mg(II)	Nitrate	100	91.9	25.30	+0.30
Mn(II)	Chloride	100	91.4	25.17	+0.17
Zn(II)	Chloride	100	90.2	24.84	−0.16
Al(III)	Acetate	100	90.7	24.98	−0.02
Cr(III)	Acetate	100	90.7	24.98	−0.02
Fe(III)*	Ferric Alum	50	91.3	25.14	+0.14
Fe(II)*	Mohr's Salt	50	90.9	25.03	+0.03
Co(II)*	Nitrate	50	90.0	24.78	−0.22
Ni(II)*	Nitrate	50	90.9	25.03	+0.03
Pb(II)*	Nitrate	50	91.4	25.17	+0.17
Cd(II)*	Sulphate	50	91.4	25.17	+0.17
Zr(IV)	Nitrate	50	91.3	25.14	+0.14
Tungstate	Sodium	50	90.9	25.03	+0.03

* Masked with EDTA.

Determination of bismuth in presence of diverse ions: The procedure for the determination of bismuth in the presence of diverse ions is the same as described above except that the *p*H of the solution was adjusted after the addition of a diverse ion. Alkali metals, alkaline earths, ammonium, Zn(II), Mn(II), Al(III), Cr(III), Zr(IV) and tungstate do not interfere with the determination and Co(II), Ni(II), Fe(II), Fe(III), Pb(II) and Cd(II) can be masked with EDTA. Ag(I), Hg(II), Cu(II) and Sb(III) interfere with the determination. The results are recorded in Table 1. The tolerance of the diverse ions has been studied only upto the amounts mentioned in the table.

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Studies on Lanthanide DAMO–SAO Mixed Complexes

V. D. Deshpande & S. S. Dara

Department of Chemistry,
Visvesvaraya Regional College of Engineering, Nagpur-440011

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SEVERAL Lanthanide simple oximates[1-5] and mixed complexes where oximes are used as primary ligands and 1,10-phenanthroline, oxine and pyridine-2, aldoxime as the second ligand were prepared and characterised[6]. This communication details the preparation and characterisation of certain Lanthanide mixed complexes using DAMO as primary ligand and SAO as second ligand.

The simple Lanthanide diacetylmonoximate were prepared by the method reported by Rao *et al.*[5]. Mixed complexes were prepared adopting the following procedure.

A weighed quantity of Lanthanide diacetylmonoximate was dissolved in ethanol and mixed with a calculated amount (Mole Ratio 1 : 3) of Salicylaldoxime. The *p*H of the solution was adjusted to 5·8 by addition of alcoholic ammonia. The resulting solution was evaporated on a steam bath when the solid separated. The excess ligand was washed with ether. All the compounds were vacuum dried over fused calcium chloride for 48 hrs. Analytical data of the mixed complexes is detailed in Table 1. The conductivity data of the compounds indicated that they are all non electrolytes.

Results and Discussion

The ligand DAMO has a band in u.v. region around 220 nm (log $\epsilon = 4{\cdot}04$) and SAO has two bands at 260 nm (log $\epsilon = 4{\cdot}22$) and 305 nm (log $\epsilon = 3{\cdot}78$). Both the ligand bands have been located in the mixed complexes with a change in log ϵ values as compared with free ligand values. The change gives an indication of the existence of both the ligands in the complexes and of their strong interaction with lanthanide ions.

In the visible region the characteristic band of Pr^{3+} and Sm^{3+} ions could not be located in this investigation. Only the 576 nm band of Nd^{3+} ion is located, with a red shift, around 580–585 nm (log $\epsilon = 1{\cdot}49$). This red shift can, as a first approximation be correlated with (i) dsp hybridisation, (ii) possible involvement of 4f electrons in chelation, and (iii) strong interaction of Nd^{3+} ion with the ligands.

In the i.r. region the ligand DAMO exhibits two bands around 3410 cm^{-1} and 3350 cm^{-1} due to OH stretch of the oxime. SAO exhibits only one band at 3350 cm^{-1} and is assigned to the presence of the oxime group with probably intramolecular hydrogen bonding. In the lanthanide salicylaldoximates reported[5] the 3350 cm^{-1} band has suffered a negative shift in some cases while it disappeared in the rest.

Table 1—Analytical data of lanthanide complexes

Complex	% Metal		% Chloride		% Nitrogen	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$Y(DAMO)_1(SAO)_1Cl_2$	22.39	22.29	17.88	17.50	6.97	6.80
$La(DAMO)_1(SAO)_1Cl_2$	31.08	30.09	15.88	15.00	6.26	6.02
$Pr(DAMO)_1(SAO)_1Cl_2$	31.37	31.20	15.82	15.60	6.23	6.20
$Nd(DAMO)_1(SAO)_1Cl_2$	31.87	31.27	15.70	15.50	6.189	5.99
$Sm(DAMO)_1(SAO)_1Cl_2$	32.78	32.50	15.48	15.40	6.105	6.08
$Gd(DAMO)_1(SAO)_1Cl_2$	33.77	33.34	15.25	15.00	6.015	6.00
$Dy(DAMO)_1(SAO)_1Cl_2$	34.52	33.90	15.09	14.95	5.95	5.80

In this investigation there is a general lowering of the OH stretch contributed by both the ligands in the 3350 cm^{-1} region. The change in intensity and lowering can be taken as an indication of N-M bond formation and also elimination of the phenolic proton of SAO during complexation.

DAMO exhibits a band around 1655 cm^{-1} due to C = O stretch. This band has disappeared in all the complexes indicating the involvement of carbonyl group in bond formation. The ligand SAO has two bands at 1620 and 1570 cm^{-1} which are due to C = N stretch. The one at 1620 cm^{-1} is slightly shifted to a higher frequency where as the 1570 cm^{-1} band could not be located in the mixed complexes. The band at 1500 cm^{-1} in SAO due to orthosubstituted benzene ring is shifted to a lower frequency and located at 1480 cm^{-1} in all the mixed complexes. The band around 975 cm^{-1} arising out of the N–O stretch of the oxime is located with slight shift in all the mixed complexes.

From an examination of the above data it can be concluded that both the ligands DAMO and SAO are involved in complexation. The oxime protons are intact whereas the proton of the phenolic OH of SAO is eliminated during complexation. General, structure assigned to the several lanthanide mixed complexes is shown in Fig. 1.

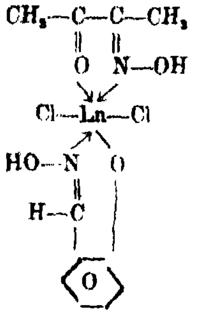


Fig. 1

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Solid State Studies on Polymerization and Depolymerization of Heteropoly Tungstate ion with Fe^{++} as the Hetero Atom

S. K. Roy & H. C. Mishra

University Department of Chemistry, Ranchi University, Ranchi-8

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A new condensation inorganic polymer, $Na_6[FeW_{12}O_{40}].28H_2O$, has been prepared and characterised on the basis of analytical and molecular weight determinations. The thermal depolymerization of the product has been studied extensively.

Of condensation of inorganic polymers[1], no reports on 12-heteropoly tungstoferrate are found in the literature. The present note is an attempt towards that line.

To 100 ml. of aqueous solution of M/5 sodium tungstate, 30 ml. of ferrous sulphate was gradually added with constant stirring at a controlled temperature of 80° in a thermostat. After half an hour interval, glacial acetic acid was added dropwise to this solution till *p*H comes just in the range of 3·5 to 3·7. The solution was boiled constantly for 6 hr., evaporated to half of its volume and allowed to crystallise in vacuo when bright needle shaped crystalline compound came out which was washed with ethanol and recrystallised thrice from hot water. Analysis of the compound was carried out by usual chemical methods and sodium was estimated by flame photometric method. (Found : Na, 3·69; Fe, 1·68; W, 62·09; H, 1·69%. Calcd. for $Na_6[FeW_{12}O_{40}].28H_2O$: Na, 3·89; Fe, 1·57; W, 62·22; H, 1·58%). Hydrogen has been analysed by element estimation method.

From the analytical data, the molecular formula of the compound, as per Kegging's view[2], comes out to be $Na_6[FeW_{12}O_{40}].28H_2O$.

Molecular weight Determinations : The cryoscopic method, as has been applied successfully by Alexander[3] and by Thilo and Krüger[4] for molecular weight determinations of polymerised silicic acids, condensed phasphates etc., in water and molten sodium sulphate decahydrate, has also been applied here for the determination of the approximate molecular weight of the compound, in the same condition i.e., in water and in molten sodium sulphate decahydrate[3,4]. This determination showed the molecular weight of the polymeric compound to be 3495 as compound with the calculated value 3544·11. To know the accurate degree of polymerization this result has been corroborated by X-ray crystal diffraction technique[5] for molecular weight determinations of heteropoly acids. The crystal diffraction data of the compound are $a = 11{\cdot}32$, $b = 14{\cdot}40$, $C = 27{\cdot}12$ Å and $\alpha = \beta = \gamma = 90°$, volume per unit cell $V = 4420{\cdot}776$ Å^3. Number of molecules per unit cell $Z = 2$. Pycnometric measurement gives the

observed density $\rho_{obs} = 2 \cdot 6$ gml^{-1}. From the relation, $\rho_{obs} = \frac{1 \cdot 66 M . z}{V}$, the molecular weight, *M*, of the compound comes to 3515 against the calculated value 3544·11.

Thermal Depolymerization: The thermal depolymerization of the compound has been studied on the light of the investigations made by West and Audrieth[6] and by Babad-Zakhryapin[7] on a few heteropoly tungstic acids. The apparatus used for this purpose was that described by Ray and Sinha[8] with continuous pumping the depolymerised product, followed by successive weighing using a theromogravimetric balance and estimations at some, stages. The dissociation[5] of the compound was observed at 75° under reduced pressure when nine molecules of water were eliminated. At 125° further eleven molecules of water were lost. The rest of the eight molecules of water remained intact in the crystal lattice till 220°, above which they were completely removed. This work agreed closely with the work of Scroggie and Clark[9] with the comparable compounds. When the temperature was raised still higher, then nearly at 350°, the compound was broken as a whole into the basic units of lower oxides of tungsten and iron which has been confirmed by analysis. So the thermal stability of 12-heteropoly tungstoferrate is 350°.

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A Test Paper Method for Detection of Sulphur Dioxide in Low Concentration by a Modified 1 : 10 Phenanthroline Reagent

Jagadeesan Nair & V. K. Gupta*

Department of Chemistry,
Ravishankar University, Raipur-492002 (M.P.), India

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1 : 10 phenanthroline has been recommended as a sensitive reagent for the determination of sulphur dioxide by Stephens and Lindstorm[1]. The method is based on the reduction of Fe(III) to Fe(II) by sulphur dioxide and subsequent measurement of coloured complex of Fe(II) and 1 : 10 phenanthroline. The method was modified by Attari *et al.*[2] by using an acetate buffer. In the present method 1 : 10 phenanthroline is used with zinc acetate and sodium nitroprusside for detection of sulphur dioxide in low concentrations. Hands *et al.* have suggested a test paper imprignated with ammoniacal zinc nitroprusside for detection and determination of sulphur dioxide[3]. A modification of this method was done by Bourbon *et al.* by using pyridine along with zinc acetate and sodium nitroprusside[4]. The method is further modified by replacing pyridine with 1 : 10 phenanthroline. It is found that the colour obtained by 1 : 10 phenanthroline is more intense. The sensitivity of the reaction is also improved considerably. The test paper impregnated with the reagents, zinc acetate, sodium nitroprusside and 1 : 10 phenanthroline is successfully used for detection of sulphur dioxide in air upto 0·5 ppm.

Experimental

Reagents: (a) 1*M* zinc acetate dihydrate in 5% v/v glycerol, (b) 1% w/v solution of sodium nitroprusside, (c) 0·2% w/v solution of 1 : 10 phenathroline in 50% aqueous ethanol.

All reagents used are of Analytical grade.

Preparation of the Test paper: Test papers are prepared by the following method—Take the above three reagents (a), (b), (c) in 10 ml beakers. Dip Whatman No. 1 filter paper strips (1×5 cms) in these solutions serially and dry the paper in a temperature controlled oven at 50–60°. These papers which are cream coloured are stable for few days if kept in well-stoppered dark bottles.

Procedure: Insert a test paper, moistened in glycerol water solution, (5% v/v) in a test paper holder and connect it to a source of suction, fitted with a rotameter. Draw one liter of air through the paper at a rate of 200–250 ml per minute. The colour of test paper turns from cream to brick red and this indicates the presence of sulphur dioxide in the sample.

Results and Discussion

By using 1 : 10 phenanthroline, the method becomes more sensitive than the methods reported by Hand[3] *et al.*, and Bourbon[3,4]. In aqueous solution the reagent gives a bulky brick red precipitate with sulphur dioxide. The coloured precipitate is sensitive to *p*H and is insoluble in common organic solvents as benzene, carbon tetrachloride, chloroform, acetone, ethanol etc. Attempts are being made to stabilise the coloured precipitate in solution and make a quantitative method for determination of sulphur dioxide, by colorimetric/turbidimetric methods.

* To whom correspondence should be made.

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Gluconate Complex of Yttrium (III)

C. PANDA and R. K. PATNAIK*

Department of Chemistry, Regional Engineering College, Rourkela-8

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Gluconate complex of yttrium has been studied by *p*H titration method. Yttrium forms a doubly charged cationic complex below *p*H 4.4 which dissociates subsequently to a cationic complex C^+ in the *p*H range 4.4 to 6.0 and finally to a neutral complex C in the *p*H range 6.0 to 8.4. The equilibrium constants of the reactions $Y^{3+}+HGl \rightleftharpoons C^{++}+H^+$, $C^{++} \rightleftharpoons C^+ + H^+$, $C^+ \rightleftharpoons C + H^+$ and $Y^{3+}+Gl^- \rightleftharpoons C^+ + H^+$ are 7.92×10^{-3}, 1.41×10^{-4}, 3.29×10^{-6} and 3.52×10^{-6} respectively.

N. A. KOSTROMINA[1,2] determined the instability constants of rare earth gluconate complexes in the *p*H range 2-3 by potentiometric and ion exchange methods.

The present paper presents the determination of stability constants of the formation of doubly charged cationic gluconate complex of yttrium at low *p*H and its dissociation to other complexes at higher *p*H.

Experimental

All chemicals used were of B. D. H. Analar grade. *p*H titrations were carried out with a Marconi *p*H meter at $32\pm1°$. The ionic strength has been maintained at $0.1M$ by the addition of suitable amount of potassium nitrate. The reaction of $Y(NO_3)_3$ with gluconic acid was found to be slow. So the solutions were stored for 48 hrs. in glass-stoppered bottles before the *p*H measurement.

Results and Discussion

The number of protons liberated during the complex formation between yttrium ion and gluconic acid remains same when the metal-ligand ratio is increased from 1 : 1.25 to 1 : 5. This indicates the formation of a 1 : 1 type of complex. The reaction taking place in experiment-1 may be represented as

$$Y^3 + HGl \rightleftharpoons C + nH^+ \quad (1)$$

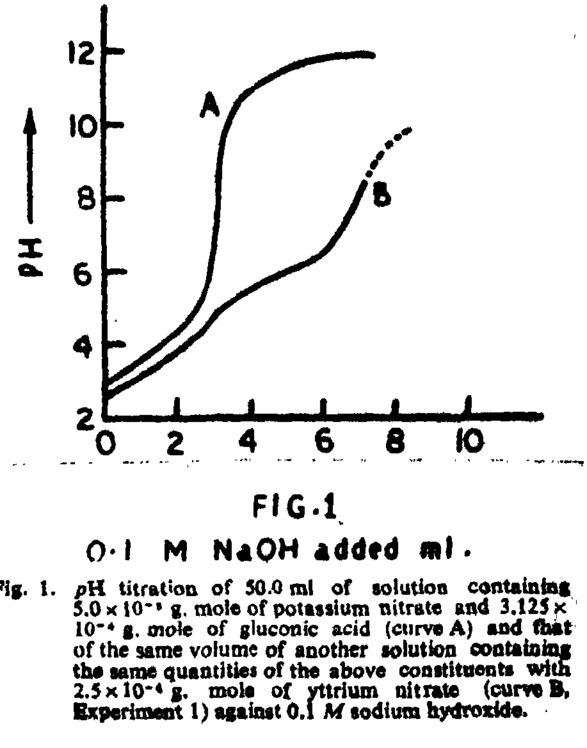
where HGl is represented by gluconic acid.

The charge of the complex C in the reaction (1) depends on the value of n, the number of protons liberated.

As derived in the cadmium citrate complex[3] and earlier investigations[4-8], it can be shown that

$$\frac{\triangle[NaOH] - a/b\ \triangle[TGl]}{[C]} = n - a/b \quad (2)$$

where $a=\frac{k}{[H^+]}$; $b=1+\frac{k}{[H^+]}$, $\triangle[NaOH]=[NaOH]_B-[NaOH]_A$ $\triangle[TGL]=[TGl]_B-[TGl]_A$; $[NaOH]_B$, $[NaOH]_A$, $[TGl]_B$, $[TGl]_A$, and [C]



FIG·1

0·1 M NaOH added ml.

Fig. 1. *p*H titration of 50.0 ml of solution containing 5.0×10^{-3} g. mole of potassium nitrate and 3.125×10^{-4} g. mole of gluconic acid (curve A) and that of the same volume of another solution containing the same quantities of the above constituents with 2.5×10^{-4} g. mole of yttrium nitrate (curve B, Experiment 1) against 0.1 *M* sodium hydroxide.

are represented by the molar concentration of Sodium hydroxide at B, sodium hydroxide at A, total gluconate at B, total gluconate at A and the complex at B respectively where B and A are two points on the curves B and A on the same *p*H axis. k, the dissociation constant of gluconic acid[9] is 2.75×10^{-4}. When the formation of the complex is complete, $[C]=[Y(NO_3)_3]$. The value of n, calculated at different *p*H, are recorded in table 1. It is >1 between *p*H 4.6 and 6.0 and >2 between

pH 6.0 and 8.4. Assuming n to be one below pH 4.60, the value of $[C^{2+}]$ is calculated. The value of the equilibrium constant K of the reaction (1) calculated by the method followed in the cadmium citrate complex[3] is found to be 7.92 x 10^{-3} against a value of 6.68 x 10^{-3} reported earlier[3] after proper conversion.

In the pH range of 4.6–6.0, n is >1 but <2 which indicates the dissociation of the complex C^{2+} by the equation

$$C^{2+} \rightleftharpoons C^{+} + H^{+} \qquad (3)$$

The equilibrium constant, K_1 of the reaction (3) is calculated as followed in the citrate complex of cadmium[3] and is found to be 1.41 x 10^{-6} (Table-1).

In the pH range of 6.0–8.4, n is >2 but <3. So the complex C^{+} dissociates by the equation

$$C^{+} \rightleftharpoons C + H^{+} \qquad (4)$$

The equilibrium constant, K_2 of the reaction (4) calculated as before is found to be 3.29 x 10^{-8} and recorded in table 1. A precipitate of yttrium hydroxide is formed at pH 8.4.

In the experiment-2, (Fig 2), the reaction taking place may be represented as

$$Y^{3+} + Gl^{-} \rightleftharpoons C^{+} + H^{+} \qquad (5)$$

where Gl^{-} is represented by gluconate ion.

The complexes C^{+} and C^{2+} exist in the pH range 4.6–6.0 as observed in experiment 1. When the pH is decreased, the complex C^{+} combines with a proton to form the complex C^{2+}. Beyond the 1 : 1 metal-ligand ratio, the pH increases due to the addition of excess sodium-gluconate and the complex C^{2+} dissociates to C^{+} and H^{+}. It can be shown as in the earlier investigations[4–5] that

$$[TGl] - [Y(NO_3)_3] = b[HGl] \qquad (6)$$

$$[C^{+}] = [H^{+}] + [HGl] \qquad (7)$$

$$\text{and} \quad [C^{2+}] = [Y(NO_3)_3] - [C^{+}] \qquad (8)$$

The equilibrium constant, K_1 of the reaction (3) is calculated as before and the mean value of K_1 is 1.04 x 10^{-6} (Table 2). This value agrees with those recorded in Table-1.

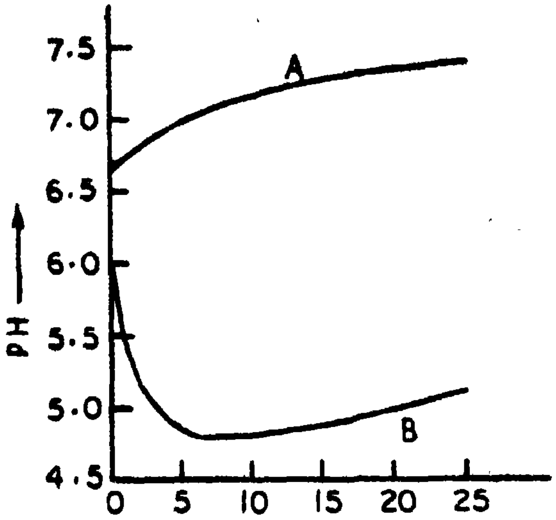


FIG. 2

0.05 M Sodium gluconate added ml.

Fig. 2. pH titration of 50.0 ml of solution containing 5.0×10^{-3} g. mole of potassium nitrate (curve A) and that of the same volume of another solution containing the same quantities of the above constituents and 2.5×10^{-4} g. mole of yttrium nitrate (curbe B, Experiment 2) against 0.05 *M* sodium-gluconate.

TABLE 1

pH	$\Delta[NaOH] \times 10^{3}$	$-\Delta[TGl] \times 10^{3}$	$[Y(NO_3)_3] \times 10^{3}$	a/b	n	$[C^{2+}] \times 10^{3}$	$[Y^{3+}] \times 10^{3}$	$[HGl] \times 10^{3}$	$K \times 10^{3}$	$K_1 \times 10^{6}$	$K_2 \times 10^{8}$
2.8	0.794	0.05	4.96	0.1797	0.342	0.979	3.981	4.283	7.23		
3.3	0.963	0.06	4.883	0.355	0.557	1.526	3.357	2.954	7.71		
3.8	0.745	0.046	4.808	0.635	0.796	2.121	2.687	1.421	8.81		
5.2	0.798	0.05	4.691	0.978	1.159					1.19	
5.4	1.235	0.078	4.664	0.986	1.267					1.43	
5.6	1.747	0.11	4.63	0.991	1.392					1.62	
7.0	5.754	0.36	4.425	0.999	2.382						6.18
7.6	6.21	0.388	4.398	1.0	2.501						2.52
8.0	6.366	0.398	4.39	1.0	2.541						1.18

TABLE 2

pH	[TGl] $\times 10^{3}$	[$Y(NO_3)_3$] $\times 10^{3}$	[HGl] $\times 10^{4}$	[C^{+}] $\times 10^{4}$	[C^{2+}] $\times 10^{3}$	$K_1 \times 10^{6}$
4.92	10.938	3.906	2.945	3.065	3.599	1.03
4.94	11.539	3.846	3.082	3.197	3.526	1.04
4.96	12.121	3.788	3.194	3.304	3.458	1.05

Below the 1 : 1 metal-ligand ratio, the ions C^{2+}, C^{+} and Y^{3+} are present. It can also be shown that

$$[HGl]=\frac{[TGl]-[H^{+}]\left(1+\frac{[H^{+}]}{K_1}\right)}{\left(1+\frac{k}{[H^{+}]}\right)+\left(1+\frac{[H^{+}]}{K_1}\right)} \qquad (9)$$

$$[C^{+}]=[H^{+}]+[HGl]$$

$$[C^{2+}]=\frac{[H^{+}]}{K_1}\ [C^{+}]$$

The equilibrium constant, K_2 of the reaction (5) calculated as before is found to be 3.52×10^{-4} (table-3).

It can be shown that $\frac{K_2 \times k}{K_1}=K$.

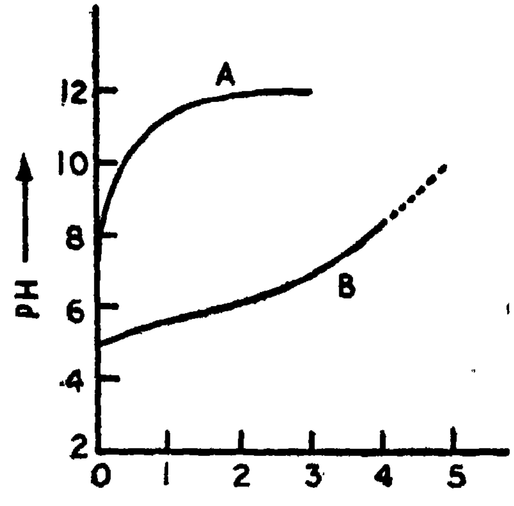
The mean value of $K_2 \times k/K_1$ is 6.9×10^{-8} which agrees well with the value of K recorded in table-1.

In the experiment-3, (Fig. 3), the metal-ligand ratio is nearly 1 : 5 and the formation of the complex is therefore assumed to be complete. It is found in the experiment-1 that complexes C^{2+} and C^{+} exist in the pH range, 4.6 – 6.0. Similarly the complexes C^{+} and C are formed between pH 6.0 and 8.4. The existence of these complexes are expected in the similar pH ranges in the experiment-3. It can be shown as in the manganese-tartrate complex[7] that

$$[C^{+}]=[H^{+}]+[NaOH]+\frac{[TGl]-[Y(NO_3)_3]}{\left(1+\frac{k}{[H^{+}]}\right)} \qquad (10)$$

TABLE 3

pH	[TGl] $\times 10^{3}$	[$Y(NO_3)_3$] $\times 10^{3}$	[HGl] $\times 10^{3}$	[C^{+}] $\times 10^{4}$	[C^{2+}] $\times 10^{3}$	[Gl^{-}] $\times 10^{5}$	[Y^{3+}] $\times 10^{4}$	$K_2 \times 10^{4}$	$K \times 10^{8}$
4.82	4.044	4.596	1.251	1.402	1.506	2.272	2.95	3.17	6.18
4.81	4.296	4.570	1.337	1.492	1.640	2.373	2.781	3.50	6.83
4.80	4.546	4.546	1.423	1.582	1.778	2.469	2.61	3.89	7.59



FIG·3

O·I. M NaOH added ml.

Fig. 3. pH titration of 50.0 ml of solution containing 5.0×10^{-3} g. mole of potassium nitrate and 1.25×10^{-3} g. mole of sodium gluconate (curve A) and that of the same volume of another solution containing the same quantities of the above constituents with 2.5×10^{-4} g. mole of yttrium nitrate (curve B. Experiment 3) against 0.1 M sodium hydroxide.

[C^{2+}] is calculated by subtracting [C^{+}] from [$Y(NO_3)_3$]. The equilibrium constant, K_1 of the reaction (3) is found to be 2.44×10^{-6} (Table-4) which is similar to the values recorded in table-1.

TABLE 4

pH	[NaOH] $\times 10^{3}$	[TGl] $\times 10^{3}$	[$Y(NO_3)_3$] $\times 10^{3}$	[C^{+}] $\times 10^{3}$	[C^{2+}] $\times 10^{3}$	$K_1 \times 10^{6}$
5.5	1.768	2.456	4.912	1.994	2.918	2.16
5.7	2.534	2.437	4.873	2.676	2.197	2.43
5.9	3.288	2.418	4.836	3.377	1.559	2.73

Similarly above pH 6.0 it can be shown as before that

$$[C]=[H^{+}]+[NaOH]-[Y(NO_3)_3]+\frac{[TGl]-[Y(NO_3)_3]}{1+\frac{k}{[H^{+}]}} \qquad (11)$$

TABLE 5

pH	[NaOH] $10^{3} \times$	[TGl] $\times 10^{3}$	[$Y(NO_3)_3$] $\times 10^{3}$	[C] $\times 10^{3}$	[C^{+}] $\times 10^{3}$	$K_3 \times 10^{8}$
7.0	6.015	2.35	4.70	1.322	3.378	3.92
7.4	6.542	2.337	4.673	1.872	2.801	2.66
8.0	7.063	2.324	4.647	2.417	2.230	1.09

[C′] is obtained by subtracting [C] from [$Y(NO_3)_3$]. The equilibrium constant, K_3 of the reaction (4) is found to be 2.56 x 10^{-3} (Table-5) which is similar to those of K_3 recorded in table-1.

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Studies in Terpenes : Part XLVII
α-Terpineol Nitrosobromide.

C. PUNNOOSE MATHEW and JAMES VERGHESE

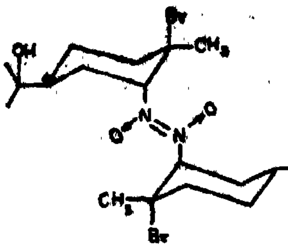
Department of Chemistry, Christian Medical College, Vellore 632002.

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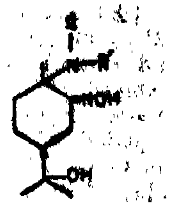
The hitherto unknown α-terpineol nitrosobromide and several nitrolamines derived therefrom are described. The N-substituent effects on the mode of chemical shift of the C_7 methyl protons of the nitrolamines detected earlier are operative in this series also.

FOLLOWING up our investigation on γ-terpinene nitrosochloride[1] we have now examined (±)-α-terpineol nitrosobromide.

On treatment with isoamyl nitrite-hydrobromic acid, (±)-α-terpineol afforded the crystalline adduct, $C_{20}H_{36}N_2Br_2O_4$, m.p. 117-118°. Based on its IR and PMR characteristics this new derivative is assigned the stereostructure (I). (The adduct is pictured as a *meso* variety though its existence as a *racemic* mixture cannot be excluded). The -NO-stretching frequencies at 11[illegible]2, 1[illegible]2 and 1226 cm^{-1} in the IR spectrum support the *trans*-dimeric configuration about the -N=N-bond.[2,3,4] The proton under the nitroso group (δ 5.88) is clearly equatorial showing only small PMR couplings to the adjacent C_6 protons. The assignment of the C_1 stereochemistry with axial bromine and equatorial methyl is based on the field position (δ 1.96) of the C_7 methyl. In a variety of 1-bromo-1-methyl cyclohexane systems it has been reported[1,5] that the equatorial methyl resonates around δ 1.98 whereas the axial methyl at about δ 1.83. The IR frequency at 710 cm^{-1} suggests an axial bromine[1]. The configurational assignment is also consistent with the free energy difference of these groups ($-\Delta G$ for methyl is 1.8 k cal/mole while $-\Delta G$ for bromine is 0.4 k cal/mole)[6]. Thus we deduce a *trans* incorporation of nitrosyl bromide across the double bond in (±)-α-terpineol.



(I)



(II)

With I as the substrate, a series of nitrolamines (II a-i), all optically inactive, were synthesised essentially as previously described for related compounds[1]. The PMR characteristics (Table I) support the assigned structures. Earlier examples of the nitrolamines originating from γ-terpinene nitrosochloride[1] have shown the chemical shift difference of the C_7 methyl with the nature of the N-substituent. Fresh evidence confirming this trend is now available. Whereas for the secondary amines II e-i the C_7 methyl resonates at δ 1.25, 1.25, 1.45 and 1.33, for the tertiary amines II a-d, these occur at the higher field at δ 0.98, 1.03, 0.98 and 1.03 respectively. This differential pattern may be accommodated by the stereochemical implication, viz., in the secondary amines the amino group is small and

TABLE 1—M.P. AND PMR δ VALUES OF NITROLAMINES

Nitrolamines® Kind	Substituents R	R'	M.P. °C	Protons H_2	C_7 Me	C_9 or C_{10} Me	N-OH
IIa	Me	Me	143-144	3.35	0.98	1.20	9.50
IIb	Et	Et	132-133	3.35	1.03	1.23	9.30
IIc	$-(CH_2)_5-$		160-161*	3.28	0.98	1.20	9.95
IId	$-(CH_2)_2$-O-$(CH_2)_2$-		190	3.35	1.03	1.22	10.00
IIe	Et	H	90	3.45	1.25	1.25	—
IIf	n-But	H	111	3.45	1.25	1.25	9.40
IIg	c-C_6H_{11}	H	139	3.42	1.25	1.25	9.20
IIh	Ph	H	155-156**	3.40	1.45	1.23	—
IIi	CH_2Ph	H	117	3.45	1.33	1.22	9.85

® Nitrolamines II a-d and II e-i have respectively (1SR, 4SR)—and (1RS, 4SR)—configurations.
* Lit.[7] m.p. 159-160°; ** Lit.[7] m.p. 155-156°.

occupies an axial position with C_7 methyl equatorial, while in the tertiary amines, the amino group is bulkier and orients equatorially, leaving C_7 methyl axial and getting itself shielded by the π-electron system[1].

Experimental

Melting points are uncorrected. Recrystallisation of II e was from benzene-petroleum ether (b. p. 40-60°) mixture and other nitrolamines, from aqueous ethanol. TLC was carried out on Merck silica gel G with methanol as solvent. All compounds were TLC pure and gave satisfactory analysis for C, H and N. PMR spectra of compounds II a, c and d were recorded in $CDCl_3$ containing trace of DMSO-d_6 and all others in $CDCl_3$.

(±)-α-Terpineol nitrosobromide : A mixture consisting of (±)-α-terpineol (4 g), isoamyl nitrite (6 ml) and ethanol (6 ml) was cooled to 0 to-10°. To this, a chilled solution of hydrobromic acid (48% aq. 4.5 ml) in ethanol (6 ml) was added dropwise with stirring over a period of 15 min. Stirring was continued for an additional 25 min and the product stood at 0–5° for 2 hr. Triturated the mass obtained with cold methanol (25 ml) and then it was collected by filtration (2 g, m.p. 115-117°). Recrystallisation from methanol afforded pure (1S, 1'R, 2S, 2'R, 4R, 4'S)-2,2'-bis-nitroso-1-chloro-8-hydroxy-p-methane (I) (1 g); m. p. 117-118° IR (Nujol): 3500, 1226, 1212, 1192 and 710 cm^{-1}; PMR: δ 5.88 (br, s, W h/2 7Hz, 1H, C_2H), 1.95 (s, 3H, C_7 Me), 1.15 (s, 3H, C_9 or C_{10} Me), 1.12 (s, 3H, C_9 or C_{10} Me).

Nitrolamines (II a-l) were prepared by the reaction of the appropriate amine with (±)-α-terpineol nitrosobromide in a manner similar to that described earlier[1]. The melting points and relevant PMR data are given in Table (1). For all nitrolamines H_{2eq} resonated as a broad doublet of J=10Hz.

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We thank Dr. T. R. Govindachari and Dr. Robert E. Lundin for IR and PMR spectra.

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Synthesis of 1,6-Bis(2-Imino-3-Allyl-4-Substituted Thiazole-N²yl) Hexane, 1,6-Bis(2-Imino-3-Allyl-4-Thiazolidinone-N²yl) Hexane and 1,6-Bis(1N-Allyl-Thiohydantoin-N³yl) Hexane.

VIJAY K. CHADHA*

Department of Chemistry, Government College, Didwana (Rajasthan).

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Condensation of N,N′ allyl hexamethylene bis-thiourea(I) with α-haloketones and chloroacetic acid in presence of anhydrous sodium acetate from II and III respectively. I when reacted with chloroacetic acid in presence of pyridine gave 1,6-bis (1N-allyl thiohydantoin-N³yl) hexane (IV).

THIAZOLES, thiazolidinones and thiohydantoins find various applications as antifungal, local anaesthetics, amoebacidal and herbicidal agents.[1-4] In continuation to our work on the synthesis of bis-thiazolidinones[5] and screening them for their antifungal and antibacterial properties, the present communication deals with the synthesis of some new bis thiazoles (II), bis-thiazolidinone (III) and bis-thiohydantoin (IV). 1,6-Diaminohexane on treatment with allyl isothiocyanate gave N, N′-allyl hexamethylene bis-thiourea (I), which when condensed with α- haloketones furnished, 1,6-bis-(2-imino-3 allyl-4-substituted-thiazole-N²yl) hexane hydrohalides (II). I on reaction with chloroacetic acid in presence of anhydrous sodium acetate, gave 1,6-bis (2-imino-3 allyl-4-thiazolidinone-N²yl) hexane (III), whereas in presence of pyridine yielded 1,6-bis (1N-allyl-thiohydantoin-N³yl) hexane (IV) respectively.

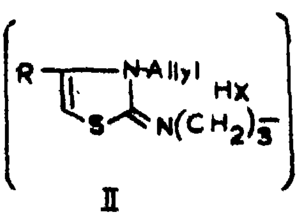
The structures of compounds II, III, and IV are in confirmity with the I. R. spectra (*vide* experimental). The lack of absorption in the region 1670 – 1700 cm^{-1} in compound II ($R = C_6H_5$) suggests the formation of a thiazole ring. III when condensed with *p*-nitrobenzaldehyde gave the arylidene derivative. The antifungal and antibacterial properties of the compounds are in progress.

Experimental

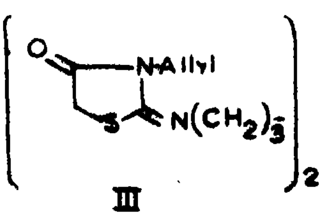
Melting points are uncorrected. Infra-red spectra were taken in Nujol mull.

N, N′-Allyl hexamethylene bis-thiourea (I): 1, 6-Diaminohexane (2.32g, 0.02 mole) was dissolved in dry benzene (20ml) and allyl isothiocyanate (4.0 g, 0.04 mole) was added drop wise and cooling under ice-cold water. A milky suspension appeared. The reaction mixture was refluxed on a steam bath for about one and a half hour. The solid thus obtained on cooling was filtered, washed repeatedly with ether and crystallized from aqueous ethanol, m p. 100 – 102°. Yield, 5.0 g(79. 5%). (Found : S,20.1 : N,17.26. Calcd. for $C_{14}H_{26}N_4S_2$: S,20 38 ; N,17.83%). ν_{max} (cm^{-1}) 1165, 1190, (C=S), 1585, 1655 (C=C, C=N), 3080 (C-H stretching), 3250 (-NH).

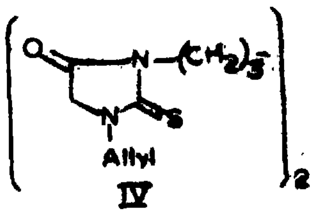
1, 6-Bis-(2-imino-3-allyl-4-phenyl thiazole-N²yl) hexane ($II, R = C_6H_5$, $X = Br$) : A mixture of I (1.04g, 0.003 mole), phenacyl bromide (1.33 g, 0.006 mole) in anhydrous ethanol (15ml) was heated under reflux on a steam bath for 4 hours. The solid separated on cooling was filtered, washed with a little ether and finally crystallised from ethanol-ether, m.p. 262-65°



II



III



IV

* Present address : Department of Chemistry, Government Post-graduate College, Churu (Rajasthan).

(decomp.). Yield 1.5 g(67.0%) (Found : S,9.15 : N,7.88. Calcd. for $C_{30}H_{36}N_4S_2Br_2$: S,9.47 : N,8.28%). ν_{max} (cm^{-1}) 700, 755 (monosubstituted benzene ring), 1590, 1630 (C=C, C=N), 3150 (-$\overset{+}{N}$H).

II(R = $-C_6H_4-C_6H_4$, X = Br) was prepared from I(1.04 g,0.003 mole), *p*-phenyl phenacyl bromide (1.84 g, 0.006 mole) and anhydrous ethanol (20ml) following the above procedure, m.p. 240° (ethanol). Yield 1.4g,(50%). (Found : S,7.38 ; N,6.64. Calcd. for $C_{42}H_{44}N_4S_2Br_2$: S,7.73 ; N,6.76%). ν_{max} (cm^{-1}) 700, 770, 840 (monosubstituted and 1,4-disubstituted benzene ring), 1590, 1605 (C=C, C=N), 3180 (-$\overset{+}{N}$H). II(R = $p-Br-C_6H_4$, X = Br) m.p. 248° (ethanol-ether). Yield 1.3 g (47%) (Found : S,7.32 ; N,6.27. Calcd. for $C_{30}H_{34}N_4S_2Br_4$: S,7,67 ; N,6 71%). II (R = $3,4(HO)_2C_6H_3$, X = Cl) 260°, (58%). (Found: S,10.09. Calcd. for $C_{30}H_{36}N_4S_2Cl_2O_2$: S,10.34%).

1, 6-Bis(2-imino-3 allyl-4-thiazolidinone-N^2*yl) hexane(III)*. A mixture of I (3.14 g,0.01 mole), monochloroacetic acid (2.0 g, 0.02 mole), anhydrous sodium acetate (2.0 g) in anhydrous ethanol (30ml) was refluxed on a steam bath for 7-8 hours. The solvent was concentrated and then poured over ice-water. A gummy solid appeared which solidified on keeping overnight. m.p. 68-70° (aqueous ethanol). Yield 2.2g (56%). (Found : S,15,97, N,13 88. Calcd. for $C_{18}H_{26}N_4S_2O_2$: S,16.25 : N,14.21%) ν_{max}(cm^{-1}) 1640, 1650 (C=C, C=N), 1715 (C=O), 3100 (C-H stretching). *5-p*-Nitro *benzylidene derivative*, m p. 172-75° (aqueous acetic acid). (Found : S,9.42. Calcd. for $C_{32}H_{32}N_6S_2O_6$: S,9.69)%.

1,6-Bis(1N-allyl-thiohydantoin-N^3*yl) hexane(IV)*: I(1.55, 0.005 mole), chloroacetic acid (1.0 g, 0.01 mole) and pyridine (6ml) were heated on a water bath for about 7-10 minutes. An exothermic reaction took place. The reaction mixture was cooled and anhydrous ethanol(15ml) was added and it was refluxed for about one and a half hour. On cooling, the solid thus obtained, was filtered, washed with a little alcohol and finally crystallized from ethanol in colourless flakes, m.p. 165° (decomp.). Yield 1.00 g(51%). (Found : S,16.33 : N,14.15. Calcd. for $C_{18}H_{26}N_4S_2O_2$: S,16.25 : N, 14.21%). ν_{max}(cm^{-1}) 1500 (C-N stretching), 1600, 1650(C=C, C=N), 1740 C=O), 3040-3140 (C-H stretching).

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Oxidative Addition Reactions of Tin(II) Oxinates*

(Miss) SUNANDA N. BHIDE, P. UMAPATHY and D. N. SEN

National Chemical Laboratory, Poona-411008.

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Bis (5,7-dichloro-8-quinolinolato) tin (II), bis (5,7-dibromo-8-quinolinolato) tin (II) and bis (5,7-diiodo-8-quinolinolato) tin (II), have been synthesized by the reaction of anhydrous $SnCl_2$ and the appropriate 5,7-disubstituted-8-quinolinol and characterised from their elemental analysis, i.r., u.v. and visible spectral data. Tin (II) bis oxinates readily react with diphenyldisulphide, PhSSPh, dibenzoylperoxide, $(PhCO)_2O_2$, iodine monochloride, ICl, halogens, etc. to yield the corresponding tin(IV) chelates. The reactions with PhSSPh and $(PhCO)_2O_2$ provide a route to the synthesis of new tin(IV) mixed ligand complexes. The i.r., u.v. and visible spectral data for some of the oxidative addition reaction products are also presented and discussed.

At present, very little is known about reactions of organotin(II) and organic tin(II) compounds. The nature of the products resulting from the direct interaction of divalent tin species with organic halides, halogens, etc. is a topic of current interest[1-3]. Although the preparations of some monomeric organic tin(II) compounds containing Sn-OC bonds[4-6], organotin compounds such as dicyclopentadienyl tin(II)[7] and their reactions with n-alkyl halides have been reported, the behaviour of tin(II) oxinates towards diphenyldisulphide, dibenzoylperoxide, iodine monochloride, halogens, etc. have not been studied. As a part of our general investigations on tin(II) chelates, it was thought worthwhile to study the oxidative addition reactions of tin(II) bisoxinate and tin(II) bis-5,7-disubstituted oxinates. The results of our investigations are presented in this paper.

Experimental

Anhydrous tin(II)chloride was prepared by dehydration of reagent grade tin(II)chloride dihydrate, $SnCl_2.2H_2O$, by reaction with acetic anhydride[8] and stored in a tightly closed ground glass bottle. Iodine monochloride and 5,7-disubstituted-8-quinolinols were prepared by the literature methods[9-12]. Solvents were purified and dried prior to use. All the other chemicals used were of reagent grade. I.R. spectra were recorded on a Perkin-Elmer Model 221 spectrophotometer. The ultraviolet and visible spectra were recorded on a Unicam S. P. 500 spectrophotometer.

1. *Bis-(8-quinolinolato)tin(II)* was prepared by the reported method[13]

2. *Bis(5,7-dichloro-8-quinolinolato)tin(II)*. Tin(II) chloride (1.89 g, 0.01 mole) dissolved in absolute alcohol (25 ml) was added with stirring to a solution of 5, 7-dichloro-8-quinolinol (4.28 g, 0.02 mole) in alcohol (250 ml). Stirring was continued for about 30 minutes and the *p*H of the mixture was adjusted to 6.0 – 6.5 by the addition of dilute ammonia (1:4) or saturated sodium acetate solution (5 g in 5 ml). The yellow precipitate formed was collected on a filter under suction, washed with alcohol and dried under vacuum. Yield, 50%. Anal. Found : C, 38.92 ; H, 1.75 ; Sn ; 21.78°/。 Calcd. for $C_{18}H_8N_2O_2Cl_4Sn$: C, 39.66 ; H, 1.469 ; Sn, 21,79°/。.

3. *Bis (5, 7-dibromo-8-quinolinolato)tin(II)* was prepared by following essentially the above experimental procedure from $SnCl_2$ (1.89 g, 0 01 mole), and 5,7-dibromo-8-quinolinol (6.06 g, 0.02 mole). The bright yellow precipitate was collected and dried. Yield, 55°/。. Anal. Found : C, 29.07, H, 1.43, Sn 16.1°/。. Calcd. for $C_{18}H_8N_2O_2Br_4Sn$: C, 29.9 ; H, 1.1 ; Sn. 16.43°/。.

4. *Bis(5,7-diiodo-8-quinolinolato)tin(II)* : Tin(II) chloride (1.89 g, 0.01 mole) in alcohol (50 ml) was added to a suspension of 5,7-diiodo-8-quinolinol(7.94 g), 0.02 mole) and the mixture was refluxed for four hours. The pale brown precipitate obtained on cooling, was collected on a filter under suction, washed with alcohol and dried. Yield, 60°/。. Anal. Found : C, 23.75 ; H, 1.28 ; Sn, 13.7°/。. Calcd. for $C_{18}H_8N_2O_2I_4Sn$: C, 23.75 ; H, 0.89, Sn, 13.04°/。.

5. *Dithiophenolato bis(5,7-dichloro-8-quinolinolato) tin(IV)*. Bis-(5,7-dichloro-8-quinolinolato) tin(II) (2.72 g, 0.005 mole) in benzene (100 ml) and diphenyldisulfide (1.09 g, 0.005 mole) in benzene (30 ml) were mixed together and refluxed for four hours. The yellow precipitate obtained was collected, washed with benzene (10 ml) and dried under vacuum. Yield, 60%. Anal. Found : C, 48.71 ; H, 3.11 ; Sn 15.3%. Calcd. for $C_{30}H_{18}N_2O_2Cl_4S_2Sn$: C, 47.2 ; H, 2.36, Sn, 15.56%.

6. *Dithiophenolato bis(5,7-dibromo-8-quinolinolato) tin (IV)* was obtained by refluxing a mixture of bis (5, 7-dibromo-8-quinolinolato) tin(II) (3.61 g, 0.005 mole) in benzene (100 ml) and diphenyldisulfide (1.09 g, 0.005 mole) in benzene (50 ml). The other experimental

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details were the same as above. Yield 60°/₀. Anal. Found : C, 38.74 ; H, 2.41, Sn, 12.3°/₀. Calcd. for $C_{30}H_{18}N_2O_2Br_4S_2Sn$: C, 38.27 ; H, 1.914 ; Sn, 12.62°/₀.

7. *Monothiophenolatotris(8-quinolinolato) tin(IV)*: Bis(8-quinolinolato) tin (II) (2.03 g, 0.005 mole) in benzene (150 ml) and diphenyldisulfide (1.09 g, 0.005 mole) in benzene (50 ml) were mixed together and refluxed. The other experimental details were the same as in 5. Yield, 40%. Anal. Found : C, 61.15 ; H, 4.08 ; Sn, 17.65 ; Calcd. for $C_{33}H_{23}N_3O_3Sn$: C, 60.02 ; H, 3.48 ; Sn, 17.99°/°.

8. *Dibenzoato-bis (8-quinolinolato)tin(IV)* Bis(8-quinolinolato)tin(II) (0.812 g, 0.002 mole) in benzene (150 ml) was added to benzoylperoxide (0.48 g, 0.002 mole) in benzene (50 ml) at room temperature. The mixture was stirred for about five hours. The solvent was removed partially under reduced pressure and the yellow precipitate formed was collected on a filter under suction and dried under vacuum. Yield 70°/₀. Anal. Found : C, 60.0 ; H, 3.81 ; Sn, 18.19°/₀. Calcd. for $C_{32}H_{22}N_2O_6Sn$: C, 59.19 ; H, 3.39 ; Sn, 18.3°/₀.

9. *Dibenzoato-bis (5, 7-dichloro-8-quinolinolato) tin(IV)* was obtained, by stirring for 4 hours, a mixture of bis(5,7-dichloro-8-quinolinolato) tin(II) (1.089 g, 0 002 mole) in benzene-dichloromethane (1:1) mixture (250 ml) and benzoylperoxide (0.48 g, 0 002 mole) in benzene (30 ml). Yield, 70°/₀. Anal. Found : C, 48 96 ; H, 2 88 ; Sn, 14.88°/₀. Calcd. for $C_{32}H_{18}N_2O_6Cl_4Sn$: C, 48.8 ; H, 2.289 ; Sn. 15.09°/₀.

10. *Dibenzoatobis (5, 7-dibromo-8-quinolinolato) tin(IV)* was obtained by stirring for 4 hours, a mixture of bis(5,7-dibromo-8-quinolinolato) tin(II) (1.45 g, 0.002 mole) in benzene-dichloromethane (1:1 mixture 300 ml) and benzoyl peroxide (0.48 g, 0 002 mole) in benzene (30 ml). Yield, 70°/₀. Anal. Found : C, 40.55 ; H, 2.24 ; Sn, 12. 18°/₀. Calcd. for $C_{32}H_{18}N_2O_6Br_4Sn$: C, 39.8, H, 1.86 ; Sn, 12.3°/₀.

11. *Dichlorobis(5,7-dichloro-8-quinolinolato)tin(IV)*: Bis(5,7-dichloro-8-quinolinolato)tin(II) (1.089 g, 0.002 mole) in dichloromethane (100 ml) was maintained at 0-5° and stirred magnetically. Wij's solution (i.e. ICl in acetic acid 0.81g in 50 ml) was added drop by drop in slight excess. Stirring was continued at this temperature for 30 minutes first and later at room temperature for 1 hour. Yellow solid separated was collected and purified by recrystallization from benzene. Yield, 60%. Anal. Found : C, 34.91 ; H, 1.64 ; Sn, 18.9%. Calcd. for $C_{18}H_8N_2O_2Cl_6Sn$. C, 34.99 ; H, 1.30 ; Sn, 19.21%.

12. *Dichlorobis(5,7-dibromo-8-quinolinolato)tin(IV)* was obtained by following the above procedure, from bis (5,7-dibromo-8-quinolinolato)tin(II) (1.45 g, 0.002 mole) in dichloromethane and ICl in acetic acid solution. Yield, 60%. Anal. Found : C,27.56 ; H. 1.5 ; Sn, 14.8%. Calcd. for $C_{18}H_8N_2O_2Br_4Cl_2Sn$: C, 27.2 ; H, 1.01, Sn, 14.97%.

13. *Monochlorotris(8-quinolinolato)tin(IV)* was obtained by following the above procedure from bis (8-quinolinolato)tin(II) (0.81 g, 0.002 mole) in dichloromethane and ICl. Yield, 40%. Anal. Found : Sn, 20.29 ; Cl ; 5.71%. Calcd for $C_{27}H_{18}N_3O_3ClSn$: Sn, 20.25 ; Cl ; 6.06%.

14. *Diiodobis(8-quinolinolato)tin(IV)*: Bis(8-quinolinolato)tin(II) (0.81 g, 0.002 mole) in methylene chloride (25 ml) was cooled (0-5°) and iodine solution (0.508 g, 0.004 mole) in methylene chloride (30 ml) was added to it drop by drop with stirring, over a period of 20 minutes. The mixture was stirred for one hour at room temperature. The solvent was removed partially under reduced pressure. The brown solid which separated out was collected on a filter, washed with methylene chloride (5 ml) and dried under vacuum. Decomposes>250°[14]. Yield, 70%. Anal. Found : C, 32.00 ; H, 1.91 ; Sn, 17.87%. Calcd. for $C_{18}H_{12}N_2O_2I_2Sn$: C, 32.71 ; H, 1.82 ; Sn, 17.97%.

15. *Diiodobis(5,7-dichloro-8-quinolinolato) tin(IV)* was obtained by following the above experimental procedure from bis (5,7-dichloro-8-quinolinolato) tin(II) (1.089 g, 0.002 mole) in methylene chloride (50 ml) and iodine (0 51 g, 0.004 mole), Yield, 65%. Anal. Found : C, 26.84 ; H, 1.48 ; Sn, 14.54%. Calcd. for $C_{18}H_8N_2O_2Cl_4I_2Sn$: C, 27 04 ; H, 1.01 ; Sn, 14.86%.

16. *Diiodobis (5,7-dibromo-8-quinolinolato tin(IV)* was obtained in the same way as above from bis (5,7-dibromo-8-quinolinolato) tin(II) (1.45 g, 0.002 mole) in methylene chloride (75 ml) and iodine (0.51 g, 0.002 mole) in methylene chloride (30 ml). Yield, 70%. Anal. Found : C, 22.4 ; H, 1.1 ; Sn, 11.98%. Calcd. for $C_{18}H_8N_2O_2Br_4I_2Sn$: C, 22.14 ; H, 0.82 ; Sn, 12.15%.

17. *Dibromobis (5,7-dichloro-8-quinolinolato) tin(IV)*: Bis(5,7-dichloro-8-quinolinolato) tin(II) (1.089g, 0.002 mole) in methylene chloride (75 ml) was cooled to 0-5°. To this solution, bromine solution (0.32 g, 0.004 mole) in methylene chloride was added drop by drop with stirring over a period of 20 minutes. The temperature of the mixture was maintained at 0-5° during this period. Stirring was continued later at room temperature for another 30 minutes. Bright yellow solid that separated out was collected on a filter, washed with methylene chloride (5 ml) and dried under vacuum. Yield, 70%. Anal. Found : C, 30 9 ; H, 1.94 ; Sn, 16.17 ; Calcd. for $C_{18}H_8N_2O_2Cl_4Br_2Sn$: C, 30.64 ; H, 1.13 ; Sn, 16.84%.

18. *Dibromobis (5,7-dibromo-8-quinolinolato) tin(IV)* was prepared by following the above experimental procedure from bis (5,7-dibromo-8-quinolinolato) tin(II) (1.45 g, 0.002 mole) in methylene chloride (75 ml) and bromine (0.32 g, 0.004 mole) in methylene chloride (30 ml). Bright yellow solid that separated out was crystallised from chloroform. Yield, 70%. Anal Found : C, 24.3 ; H, 1.1 ; Sn, 13.3°/₀. Calcd. for $C_{18}H_8N_2O_2Br_6Sn$: C, 24.47 ; H, 0.9 ; Sn, 13.45°/₀.

19. *Monochloro(8-quinolinolato) tin(II)*[18]: Tin(II) chloride (1.89 g, 0.01 mole) dissolved in absolute alcohol (25 ml) was added to a solution of bis (8-quinolinolato) tin(II) (4.06 g, 0.01 mole) in benzene and the mixture was refluxed for four hours. The pale yellow precipitate obtained on cooling was collected on filter under suction, washed with alcohol and benzene and dried. Yield, 90%. Anal. Found : C, 36.1 ; H, 2.32 ; Sn, 39.78%. Calcd. for $C_9H_6NOClSn$: C, 36.21 : H, 2.01 ; Sn, 39.8%.

20. *Monochloro (5,7-dichloro-8-quinolinolato) tin(II)* was obtained by following the above experimental procedure, from bis (5,7-dichloro-8-quinolinotato) tin(II) (0.55g, 0.001 mole) in benzene (250 ml) and tin(II) chloride (0.189 g, 0.001 mole) in absolute alcohol. Yield, 70%. Anal. Found : C, 29.7 ; H, 1.51 ; Sn, 32.43%. Calcd. for $C_9H_4NOCl_3Sn$: C, 29.4 ; H, 1.09 ; Sn, 32.32%.

21. *Monochloro (5,7-dibromo-8-quinolinolato) tin(II)* was obtained in the same manner as above from bis (5,7-dibromo-8-quinolinolato) tin(II) (0.73 g, 0.001 mole) in benzene (200 ml) and tin(II) chloride (0.19 g, 0.001 mole) in absolute alcohol. Yield, 65%. Anal. Found : C, 23.49%. H, 1.16 ; Sn, 26.3% Calcd. for $C_9H_4NOBr_2ClSn$: C, 23.71 ; H, 0.87 ; Sn, 26.06%.

Results and Discussions

The reactions of tin(II) chelates, bis(8-quinolinolato)-tin(II), bis(5,7-dichloro-8-quinolinolato) tin(II) and bis(5,7-dibromo-8-quinolinolato) tin(II), with diphenyldisulphide, PhSSPh, proceed smoothly in refluxing benzene medium to afford initially the oxidative addition product, $SnL_2(SPh)_2$, which equilibrates to give, in addition, the disproportionation products, SnL_3SPh and $SnL(SPh)_3$. The reaction may be schematically represented as follows :

$$SnL_2 + PhSSPh \rightarrow SnL_2(SPh)_2 \rightleftarrows SnL_3(SPh) + SnL(SPh)_3$$

where HL is 8-quinolinol or 5,7-dichloro-8-quinolinol or 5,7-dibromo-8-quinolinol. However, Sn(II) substituted chelates yielded the addition products, $SnL_2(SPh)_2$ while the reaction of bis(8-quinolinolato) tin(II) afforded the disproportionation product, $SnL_3(SPh)$. Similar reactions have been cited in literature. In a preliminary communication Bos et al.[15] have reported the reaction of bis (cyclopentadienyl) tin(II) and diphenyldisulphide to give similar oxidative addition and disproportionation products. 3,4-Dithiolatotolyltin(II) similarly, is immediately oxidised by further 3,4-dithiotoluene to yield bis(3,4-dithiolatotolyl) tin(IV)[16].

Recently it has been shown that bis (cyclopentadienyl) tin(II) is readily oxidized by halogens to give $(C_5H_5)_2SnHal_2$[16]. However, Noltes and his coworkers[16] have pointed out that this reaction is more complicated and demonstrated the transient formation of $(C_5H_5)_2\overset{IV}{Sn}I$, $(C_5H_5)\overset{II}{Sn}I$ and $C_5H_5\overset{IV}{Sn}I_3$ upon addition of I_2 to a $(C_5H_5)_2Sn$ solution at room temperature. Tin(II) oxinates were readily oxidized by iodine to give the corresponding Sn(IV) chelates, SnL_2I_2. Upon bromine addition the tin(II) substituted oxinates only afforded the dibromo-Sn(IV) chelates, SnL_2Br_2. The bis(8-quinolinolato) tin(II) gave only an impure product. Direct chlorination, similarly, of bis(8-quinolinolato) tin(II) resulted in the isolation of an insoluble red, probably, polymeric product. Interestingly, chlorination of the chelates could be effected by another route, namely, by the reaction of a slight excess of iodine monochloride, ICl, in acetic acid solution.

On addition of a slight excess of an acetic acid solution of ICl, at room temperature to a solution of tin(II) chelates in alcohol or dichloromethane and stirring for 2 hrs. corresponding dichloro bis(substituted-8-quinolinolato) tin(IV) compounds were obtained. Bis(8-quinolinolato) tin(II), however, gave monochlorotris(8-quinolinolato) tin(IV), presumably due to disproportionation

$$SnL_2 + ICl \rightarrow SnL_2Cl_2 \rightleftharpoons SnL_3Cl + SnLCl_3$$

This compound appears to be rather unstable. According to ionic hypothesis, iodine monochloride is partially ionized and chlorine oxidative addition reaction can take place by this mechanism or that iodine monochloride behaves towards certain metals including tin, very much like chlorine forming the metal chloride, some iodide and free iodine[17] and further reactions of the metal chloride would result in the chlorinated product. Tauzher et al.[18,19] have recently investigated the reactions between alkyl and aryl bis(dimethyl glyoximato) cobalt(III) and ICl in chloroform and observed that in the absence of excess of added chloride ion [added as $(CH_3)_4NCl$], the reactions proceed via electrophilic substitution mechanism, in presence of an excess of chloride ion, both oxidative dealkylation and radical attack can occur.

Addition of a solution of benzoyl peroxide in dry THF (or benzene + dichloromethane) to a stirred solution of tin(II) chelates in dry THF or (C_6H_6+ CH_2Cl_2) resulted in a rapid reaction leading to the formation of bis(oxinato) Sn(IV) dibenzoates

$$SnL_2 \xrightarrow{(PhCO)_2O_2} L_2Sn(OOCPh)_2$$

(HL = 8-quinolinol or 5,7-dichloro-8-quinolinol or 5,7-dibromo-8-quinolinol)

Harrison and Ewings[2] have reported the isolation of tin(IV) dihalide dibenzoates by the reaction (exothermic) of dibenzoylperoxide at room temperature with tin(II) halides.

Sn(II) oxinates also readily undergo disproportionation reactions with tin(II) chloride to give three coordinate divalent tin compounds, SnLCl

$$SnL_2 + SnCl_2 \rightarrow 2SnLCl$$

(HL = 8-quinolinol or 5,7-dichloro-8-quinolinol or 5,7-dibromo-8-quinolinol)

In these reactions the tendency for the tin atom to achieve three coordination is apparently maintained. The quinolinol moiety presumably occupies two coordination positions characteristic of chelate formation with chlorine atom in the third position. Curran and Doskey[30] from their Mössbauer spectral studies concluded that the tin atom in SnCl(oxine) is probably three coordinate (Fig. I) as there is no evidence for halogen bridging to give a higher coordination number than three.

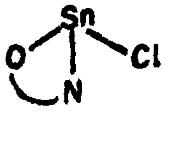
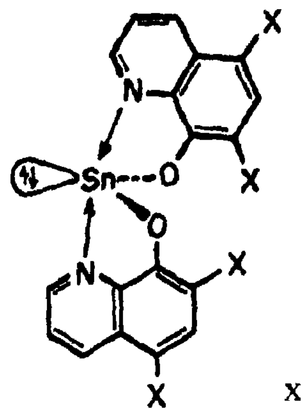


FIG. I.

On this basis, the tin atom in monochloro(5,7-dihalo-8-quinolinolato) tin(II) chelates is probably three coordinate. In the i.r. spectra of 8-quinolinol and 5,7-dihalo-8-quinolinols the broad to medium intensity band observed at ca. 3200 cm^{-1} may be attributed to inter/intra molecularly bonded OH vibration. The phenolic OH in-plane deformation vibration coupled with C-O str. mode is observed at ca. 1410 cm^{-1} and at ca. 1200 cm^{-1}. The second coupled mode expected at ca. 1200 cm^{-1} could be also located in all the substituted 8-quinolinols. The absence of these absorption bands in the spectra of the chelates, bis(8-quinolinolato) tin(II), bis(5,7-dichloro-8-quinolinolato) tin(II), bis(5,7-dibromo-8-quinolinolato) tin(II) and bis(5,7-diiodo-8-quinolinolato) tin(II), indicates that the proton of the hydroxyl group is replaced by the metal in the chelates. Charles et al[31] have measured the i.r. spectra of metal-8-quinolinol complexes and have shown that the aryl-oxygen vibration appearing at 1090 cm^{-1} in 8-quinolinol, shifts to higher frequency on chelation and is attributed to the formation of an M – O – C system. The i.r. spectra of tin(II) chelates with 8-quinolinol and 5,7-dihalo-8-quinolinol show this characteristic vibration at ca. 1100 cm^{-1}. This indicates that both 8-quinolinolato moieties in these chelates, function as bidentate ligands, apparently increasing the coordination number of tin atom to four. Divalent tin compounds are generally expected to achieve coordination saturation at coordination number three[22] as in tin(II) sulphate[23] or potassium tris (formato) stannate(II)[24] which have pyramidal three-coordinate tin. However, more recent structural investigations on tin(II) oxygen compounds show that simple trigonal-pyramidal geometry for tin(II) is by no means exclusive and coordination number at tin(II) can increase beyond three[25-27]. In tin(II) β-diketonato derivatives it was assumed on the basis of available structural data[28,29] that β-diketonate functions as an intramolecularly coordinating bidentate ligand and the tin atom in the compounds is expected to be four-coordinate. In analogy with tin(II) β-diketonato complexes as well as bis(diethyldithiocarbamato) tin (II)[30], the probable structure for the tin(II) bisoxinates is likely to be a distorted trigonal bipyramid at tin in which the tin lone pair exhibits stereochemical activity, occupying an equatorial position viz.



X = H or a halogen

FIG. II

The i.r. spectra of tin (II) bisoxinates in the region 700 cm^{-1} – 300 cm^{-1} are complicated due to the absorption bands of the ligands. However, two new absorption bands which are absent in the spectra of the ligands are observed in the 450-500 cm^{-1} region and at ca. 330 cm^{-1}. The Sn-Oxygen stretching frequency is not generally readily assignable. In Sn(II) chelates investigated recently, strong to medium intense bands observed in the i.r. spectra at ca. 490-515 cm^{-1} have been assigned to ν(Sn-O) vibrations[31]. The intense band observed in the spectrum of tin(II) methoxide at 560 cm^{-1} has been assigned by Harrison to ν(Sn-O) vibration[32]. Accordingly, the strong to medium intense bands present in the spectra of bis(8-quinolinolato) tin(II) and bis(5,7-dihalo-8-quinolinolato)tin(II) have been ascribed to ν(Sn – O) vibrations. Of considerable interest would be the frequency of tin-nitrogen coordinate bond stretching mode in Sn(II) chelates. The medium to weak intensity absorption bands observed at ca. 330 cm^{-1} have been tentatively assigned to ν(Sn←N) vibrations in analogy with recent assignments by Nakamoto in some tin(II) complexes contain ing tinnitrogen bond[33].

The Sn-Cl symmetric and anti-symmetric stretching modes of the bent triatomic $SnCl_2$ observed in the i.r. spectrum at ca. 350 cm^{-1} and at ca. 330 cm^{-1} respectively, on complex formation shift slightly to lower frequencies. The magnitude of the shift is of the order of ~7 cm^{-1}. In the spectra of monochloro oxinato-tin(II) chelates, SnLCl, the weak brohad bands observed at ca. 322 cm^{-1} may be attributed to antisymmetric Sn – Cl str. vibration. The symmetric Sn – Cl str. vibration apparently is masked due to the presence of other vibrations. The Sn – Br and Sn – I vibrations in the spectra of Sn(IV) chelates could not be located, for the spectra were recorded upto 300 cm^{-1} only.

TABLE 1—ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA OF TIN(II) AND TIN(IV) CHELATES WITH 8-QUINOLINOL AND SUBSTITUTED 8-QUINOLINOLS.

S. No.	Compound	Solvent	λ_{max} (nm)	$\epsilon(M^{-1}cm^{-1}) \times 10^{-3}$
1.	8-Hydroxyquinolinol	Methanol	310	2.39
			256	
			231	
	-do-	CCl_4	320	2.64
2.	5,7-Dichloro-8-quinolinol	$CHCl_3$	337	3.00
3.	5,7-Dibromo-8-quinolinol	$CHCl_3$	337	3.00
4.	5,7-Diiodo-8-quinolinol	Alcohol	335	1.9
5.	$Sn(Ox)_2$	Methanol	375	0.85
	do-	D. M. F.	380	2.25
	-do-	CH_2Cl_2	385	2.35
	-do-	Benzene	395	1.35
6.	$Sn(dichloroOx)_2$	Benzene	420	
		CCl_4	410	3.6
		Methanol	265	
			250	
7.	$Sn(dibromoOx)_2$	Benzene	415	4.27
		Methanol	255	
			265	
8.	$Sn(diiodoOx)_2$	DMF	400	3.53
9.	$Sn(dichloroOx)_2Cl_2$	Benzene	420	3.93
10.	$Sn(dibromoOx)_2Cl_2$	-do-	420	2.97
11.	$Sn(OX)_2Cl$	-do-	417	5.83
12.	$Sn(dichloroOx)_2Br_2$	do-	415	3.66
13.	$Sn(dibromoOx)_2Br_2$	-do-	420	1.26
14.	$Sn(dichloroOx)_2I_2$	-do-	410	3.64
15.	$Sn(dibromoOx)_2I_2$	Benzene	415	5.89
16.	$Sn(oxine)_2I_2$	-do-	395	2.09
17.	Sn(Ox)Cl	Methanol	243	2.7
		-do-	257	2.6
		DMF	390	2.39
18.	Sn(dibromoOx)Cl	Benzene	415	2.3
19.	Sn(dichloroOx)Ci	Benzene	412	1.525
		Methanol	267	4.35

* HOx = 8.quinolinol

The ultraviolet and visible absorption spectral data for the tin chelates along with the ligands are presented in Table 1. The absorption bands of the anion of 8-quinolinol and some of its chelates have been assigned by Perkampus and Körtum[64] and according to these authors the absorption band appearing at 322 nm is the low energy transition and the one at 317.5 nm is the high energy transition. The shift to longer wave lengths of 320 nm absorption of 8-quinolinol in the spectra of oxinatometal complexes is generally considered to be a reliable indication for the presence of a chelating oxine ligand[34-37]. In the U.V. and visible spectra of tin(II) bisoxinates as well as in dihalogenobis(oxinato or substituted oxinato)Sn(IV) chelates, the low-energy absorption band in the ligands (ca. 320-340 nm) is shifted to ca. 375-420 nm and is observed as a strong broad band indicating the presence of chelated 8-quinolinolato or substituted 8-quinolinolato groups in the compounds. The strong band observed at ca. 265 nm in the chelates and also in the ligands is mainly due to the benzene ring vibrations[34,38].

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A Novel and Convenient Synthesis of N-Phenylbenzohydroxamic Acid (PBHA)

B. S. CHANDRAVANSHI and V. K. GUPTA*

Department of Chemistry, Ravishankar University, Raipur, M. P., India.

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A one step process for the preparation of N-phenylbenzohydroxamic acid has been developed. The method yields PBHA of moderately high purity in short reaction time.

N-Phenylbenzohydroxamic acid, abbreviated as PBHA, is prepared in one step by reduction of nitrobenzene with zinc and acetic acid and simultaneously reacting N-phenylhydroxylamine thus formed with benzoyl chloride in diethyl ether, at low temperature. PBHA obtained has been characterized by melting point, ultra violet absorption spectra, and molar absorptivity with vanadium(V). The method proposed here is fast, cheap and gives satisfactory yield as compared to other reported methods. All previously reported synthesis of PBHA required freshly prepared and crystallized phenylhydroxylamine, which was dissolved in hot water or diethyl ether and then reacted with benzoyl chloride at different temperatures in different alkaline mediums[1-9]. All methods described are essentially two step preparation involving a lot of solvent, and long reaction time (about 5 hours) and conversion to PBHA in terms of nitrobenzene is also low. By the method described here the time is reduced to less than one hour and yield of PBHA is also improved (about 60%) with respect to nitrobenzene.

Experimental

12.3 g. (0.1 mole) of nitrobenzene, 15 ml. (approx. 0.2 mole) of glacial acetic acid and 15 ml. ice cold water are taken in a 250 ml. three necked flask, fitted with a mechanical stirrer and separatory funnel. The flask is kept in a freezing mixture. 7 g. (approx. 0.1 mole) of zinc dust are taken. Assuming 60% conversion of nitrobenzene into phenylhydroxylamine, 8.4 g. (0.06 mole) of benzoyl chloride dissolved in 25 ml. diethyl ether is transferred into the separatory funnel. Zinc dust and benzoyl chloride are added to the contents of the three necked flask, slowly with vigorous stirring in the course of about 20 minutes. Temperature is maintained below 2°. As the nitrobenzene gets reduced to phenylhydroxylamine by zinc and acetic acid, it reacts with benzoyl chloride to produce N-phenylbenzohydroxamic acid, which gets precipitated in the course of reaction. After the reaction, this is filtered along with the unreacted zinc dust. From the filtrate ethereal layer, if present, is separated and ether distilled off. The yellowish white solid obtained from the ethereal layer is combined with the rest of residue and treated with 20-25 ml. concentrated hydrochloric acid to dissolve out the unreacted zinc dust. The solution is cooled and treated with 50ml. of cold water. The PBHA is filtered, and crystallized from benzene petroleum ether. Two to three recrystallizations give pure product, m.p. 121° (Reported value 121°)[9]. Yield 70 to 80%. Molar absorptivity of its vanadium(V) complex in chloroform at 530 nm is 4650±50 liter/mole cm. (Reported 4650±50)[10]. Ultraviolet spectra are taken in 95% spectroscopic ethanol in UV VIS Specord, $\lambda max = 268$ nm, $\epsilon = 8900 \pm 50$ l. $mole^{-1} cm^{-1}$ (Reported $\lambda max = 268$ nm, $\epsilon = 8900 \pm 50$ l. $mole^{-1} cm^{-1}$)[9].

Note: 1. Higher temperature (even room temperature) and longer addition time of benzoyl chloride yields other products (benzanilide m.p. 163°) from which PBHA is separated with difficulty.

2. Excess of benzoyl chloride and zinc dust give low yield.

3. Presence of excess phenylhydroxylamine is tested with Tollen's reagent after the reaction. If it is still present, then excess benzoyl chloride is added as described in above procedure.

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* To whom correspondence should be made.

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Molecular Adsorption of Carboxylic Acids by Anion-Exchange Resin

L. POCHHALI* and S. K. ADHIKARY

Physical Chemistry Section, Jadavpur University, Calcutta-700032

and

K. C. RAY

Department of Chemistry, Visva-Bharati, Santiniketan, Birbhum, West Bengal, India

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Pure molecular adsorption of carboxylic acids (formic to n-butyric), mono- and dichloroacetic acids and hydrochloric acid has been studied with an anion-exchange resin, Amberlite-IRA-400, in its respective anion forms. The order of molecular adsorption of these acids on the respective anion forms of the resin is, hydrochloric < formic < acetic < propionic < n-butyric < monochloroacetic < dichloroacetic. For the carboxylic acids, molecular adsorption increases with the increase in chain length of the acids.

The adsorption of the strong acid, HCl, is very small. Also it is known that not the carboxylate ions but the undissociated acids are molecularly adsorbed by the resin. But here it is found that the molecular adsorption of the chlorosubstituted acetic acids is considerably higher than the carboxylic acids studied, though the dissociation constants of the chlorosubstituted acetic acids are much greater than those of the carboxylic acids.

Molecular adsorptions of the carboxylic acids by the nitrate, sulphate and chromate forms of the same resin have also been studied. The order of molecular adsorption of these acids by all the salt forms of the anion-exchange resin is the same as obtained for the resin containing the same counter-anions as the acids. The acids are most strongly held by the chromate form of the resin and least strongly by the nitrate form.

SYNTHETIC ion-exchange resins have got the property of adsorbing molecules of non-electrolytes as well as electrolytes, specially weakly dissociated electrolytes like aliphatic carboxylic acids. But in the latter case both ion-exchange and molecular adsorption take place simultaneously, when counter-ion of the resin is different from that in the acid. Some works on adsorption of these acids on cation-exchage resins have been reported by Reichenberg and Wall[1]; Starobinets and Kharevich[2] and others[3-5]. Like cation-exchange resins, weak and strong electrolytes are adsorbed by anion-exchange resins. Molecular adsorption of carboxylic acids by anion-exchange resins has been studied recently by Starobinets et al[6-10]. Molecular adsorption of fluoroacetic acids together with acetic acids by anion-exchange resin in its respective ionic forms, have been studied by Samuelson, Soldatov and Thornton[11].

Pure molecular adsorption occurs when solution of a particular electrolyte comes in contact with an anion-exchange resin containing counter-ion similar to that present in the electrolyte. In the other forms ion-exchange together with molecular adsorption may also occur. If the resin in R-X form (X is anion of an acid) is equilibrated with an acid of the type HA, then ion-exchange occurs between X^- and A^- in the following way,

$$R-X+HA \rightleftharpoons R-A+HX.$$

The decrease in concentration of HA due to ion-exchange is equal to the concentration of the new acid (HX) formed. Hence total concentration of acids in the equilibrium solution will be the same as initial concentration of the acid HA. Any decrease in concentration observed in the equilibrium solution will give the value of molecular adsorption which can be determined from the difference in concentrations of the acids.

In this paper, molecular adsorptions of carboxylic acids, formic to n-butyric, mono- and dichloroacetic and hydrochloric acids by an anion-exchange resin, Amberlite-IRA-400, containing counter-ions similar to those in the acids, have been studied. Similar studies have also been done with formic to n-butyric acids and the same anion-exchange resin in nitrate, sulphate and chromate forms.

* Senior author

Experimental

A monofunctional highly basic quaternary alkylammonium polystyrene resin, Amberlite-IRA-400, cross-linked with 8% divinylbenzene was obtained commercially (manufacturer : Rohm and Haas Co., U.S.A.) in spherical beads. The resin in chloride form was first washed with double distilled water and then transferred into a column. The resin was then converted into OH-form by thorough leaching with about 0.5 *N* NaOH solution. Leaching was continued till the effluent gave no test for chloride with $AgNO_3$ solution. The resin was then completely washed with double distilled water until the effuent gave no colour with phenolphthalein. The hydroxyl form of the resin was then air-dried at room temperature.

The carboxylates, chloro-acetates, chloride, nitrate and sulphate forms of the resin were prepared from the hydroxyl form by treating with about 1*N* of corresponding acids and then washed carefully with double distilled water to remove the additional acids from the resin. These were checked by conductometric and *p*H measurements of the efluents. These were then air-dried and kept in closed containers.

The chromate form of the resin was prepared from the hydroxyl form by treating with about 1*N* K_2CrO_4 solution and then washed free from excess K_2CrO_4 with double distilled water, air-dried and kept in a closed container.

Aliphatic acids ranging from formic to n-butyric, mono- and dichloroacetic acids, hydrochloric acid were obtained in pure "analar grades" and so used without any further purification.

Before doing the experiments, the exchange capacity of the resin was found out. The exchange capacity of the resin was determined by two methods ; (i) A weighed amount of hydroxyl form of the resin (about 1 gm.) with known moisture content was equilibrated with 0.2*N* HCl solution in a stoppered Jena glass bottle by shaking in a mechanical shaker for 4 hours. The mixture was then kept for 24 hours to attain equilibrium. The solution was then separated from the resin and the unreacted acid was titrated with standard sodium hydroxide solution using phenolphthalein indicator. The amount of acid consumed in the reaction with the resin was obtained by difference in concentrations. This difference gave the exchange capacity of the resin. (ii) In the second method, a weighed quantity of the resin (about 1 gm) in chloride form was taken in a column. About 1*N* NaOH solution was passed through the column. Liberated chloride was estimated by argentometric titration with $AgNO_3$ solution using fluorescein as an indicator[12]. The exchange capacity per gm of dry resin was calculated from the amount of chloride ion displaced. From these two methods the exchange capacity of the resin, Amberlite-IRA-400, was found to be 2.52±0.02 meq per gm of dry resin.

For determining the molecular adsorption, known amounts (about 1 gm) of the air-dried resin in different salt forms of known moisture content were equilibrated with 50 ml acid solutions of known initial concentrations. In the case of chromate form of the resin, the colour of the resin changed from yellow to orange after adding acid solutions to the resin. This showed that in acid solution, the CrO_4^{2-} ion of the resin was converted into $Cr_2O_7^{2-}$ ion. But for simplicity the term "chromate-resin" will be used in this paper. The mixtures were shaken in a mechanical shaker for 4 hours and then kept for 48 hours to attain equilibrium. The concentrations of the equilibrium solutions were found out by alkalimetric titration using phenolphthalein indicator. In the case of sulphate form of the resin, an attempt was made to estimate the exchanged SO_4^{2-} ion in the equilibrium solution by titrating it with standard $BaCl_2$ solution using Na-Rhodizonate adsorption indicator[12]. But concentration of SO_4^{2-} ion was so low that it could not be estimated by this method.

For the chromate form of the resin, the equilibrium acid solutions were completely colourless, whereas it was found that $K_2Cr_2O_7$ solution, even at so low a concentration as 0.0001N, shows a distinct colour. This indicates that even if any dichromate ion is present in the solution due to ion-exchange, its concentration must be less than 0.0001N, which would give the ion-exchange value less than 0.005 meq per gm of dry resin.

In the case of nitrate form of the resin, the estimation of exchanged ion was not attempted due to non-availability of any simple suitable analytical method for its estimation.

The molecular adsorption of an acid was calculated from the difference between initial and final concentrations of the acid.

All the experiments were done in room temperatures (30±2°).

Results and Discussions

Molecular adsorption isotherms of the acids (i.e ; formic, acetic, propionic, n-butyric, mono- and dichloroacetic acids and hydrochloric acid) on the respective anion forms of the Amberlite-IRA-400, are presented in figure 1. It is found that, molecular adsorption increases in the order, HCl $<$ formic $<$ acetic $<$ propionic $<$ n-butyric $<$ monochloroacetic $<$ dichloroacetic. The order of molecular adsorption for the carboxylic acids is a function of the chainlength of the acids. The result is in agreement with the findings of Schneider, Kresheck and Scheraga[13], who evaluated the thermodynamic parameters for the adsorption of carboxylic fatty acids on a hydrocarbon network polystyrene. Their data indicate that the molecular adsorption of hydrocarbon chains of fatty acids takes place by a mechanism involving a decrease in the structure of water. But if the structure breaking of water is the

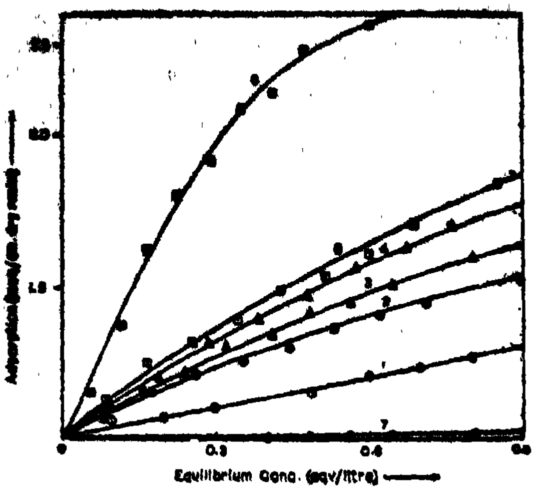


Fig. 1. Adsorption Isotherms of acids on the corresponding anion forms of Amberlite-IRA-400.

1. Formic acid on formate form., 2. Acetic acid on acetate form., 3. Propionic acid on propionate form., 4. n-butyric acid on n-butyrate form., 5. Mono chloro acetic acid on monochloro-acetate form., 6. Dichloro acetic acid on dichloro acetate form., 7. HCL on chloride form.

only cause for increasing adsorption with increase in chainlength, the large adsorption of mono- and dichloroacetic acids can not be explained. The same authors[1] found that in homologous series of acids ranging from formic to n-butyric, only the undissociated form of the acids and not the dissociated carboxylate anions are adsorbed from aqueous solutions. The adsorption of the strong acid, i.e ; HCl, is also very small. The dissociation constants[15] of monochloro- and dichloroacetic acids are 1.40×10^{-3} and 3.32×10^{-2} respectively, whereas that of acetic acid is 1.76×10^{-5}. From the standpoint of both structure breaking property, as well as dissociation constant, the adsorption of chlorosubstituted acetic acids should have been smaller than acetic acid. Samuelson, Soldatov and Thornton[11] observed large adsorptions of fluro-acetic acids on the corresponding anion forms of an anion-exchange resin. They explained the large adsorptions of fluoro-acetic acids from the point of view of formation of hydrogen bonding of nondissociated acids to the counter-ions inside the resin. Possibly the same mechanism is responsible for the large adsorption of the chloro-acetic acids.

Molecular adsorption isotherms of the carboxylic acids (i.e., formic to n-butyric) by the sulphate and chromate forms of Amberlite-IRA-400, are given in figures 2 and 3. From these figures, molecular adsorptions are seen to increase in the order, formic< acetic<propionic<n-butyric for both the salt forms of the resin. In these salt forms of the resin, simultaneous ion-exchange and molecular adsorption might have been expected. But, as mentioned earlier, the ion-exchange was found to be almost nil within experimental error. This indicates that ion-exchange is not favoured by the anion-exchange resin containing multivalent counter-ion. The counter-ion associates

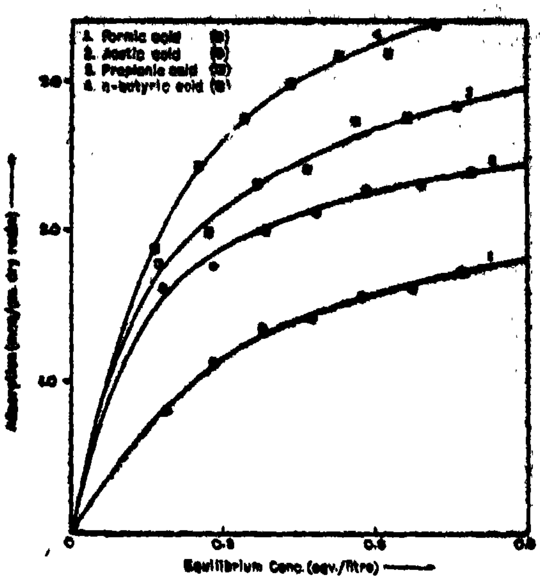


Fig. 2. Adsorption Isotherms of Carboxylic acids on the Sulphate form of Amberlite-IRA-400.

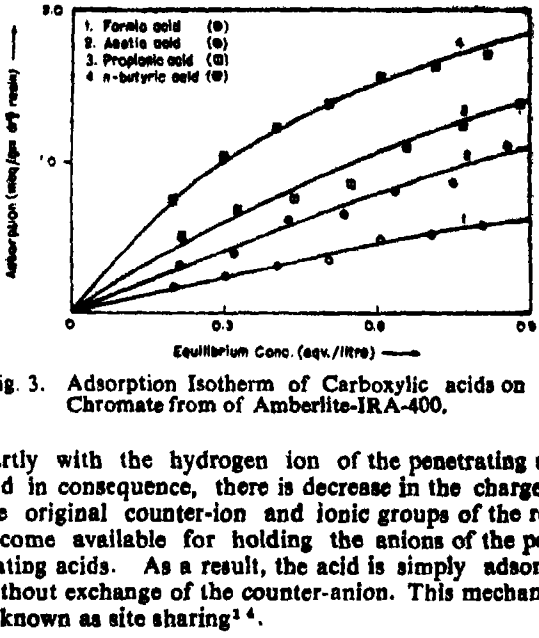


Fig. 3. Adsorption Isotherm of Carboxylic acids on the Chromate from of Amberlite-IRA-400.

partly with the hydrogen ion of the penetrating acid and in consequence, there is decrease in the charge of the original counter-ion and ionic groups of the resin become available for holding the anions of the penetrating acids. As a result, the acid is simply adsorbed without exchange of the counter-anion. This mechanism is known as site sharing[14].

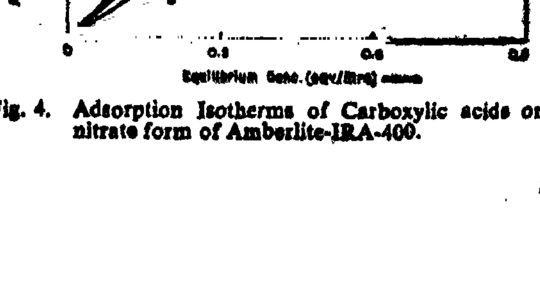


Fig. 4. Adsorption Isotherms of Carboxylic acids on the nitrate form of Amberlite-IRA-400.

With the *nitrate form of the resin*, the same order of molecular adsorption for the carboxylic acids have *been found, as is shown in figure 4.*

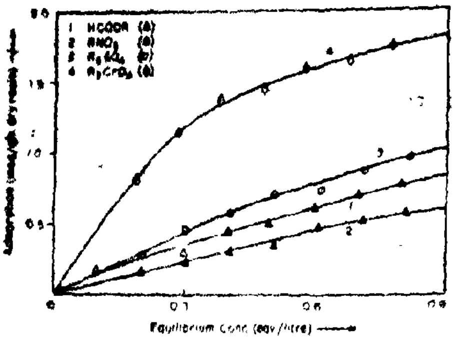


Fig. 5. Molecular adsorption Isotherms of formic acid on Amberlite-IRA-400.

Ion-exchange isotherms of formic acid by the various resin salts are shown in fig. 5. For all other acids similar graphs can be shown. From these graphs, following results are obtained.

TABLE—1

Acids	*Order of molecular adsorption*
Formic	: $RNO_3 < HCOOR < R_2SO_4 < R_2CrO_4$
Acetic	: $RNO_3 < CH_3COOR < R_2SO_4 < R_2CrO_4$
Propionic	: $RNO_3 < CH_3CH_2COOR = R_2SO_4 < R_2CrO_4$
n-butyric	: $RNO_3 < R_2SO_4 < CH_3CH_2CH_2COOR < R_2CrO_4$
	R—Resin matrix.

It is found that all the acids are most strongly held by the chromate form and most weakly by the nitrate form of the resin. For formic, acetic, propionic acids, position of the respective carboxylate form of the resin lies between nitrate and sulphate forms, whereas in the case of n-butyric acid, the position of the n-butyrate form is between sulphate and chromate forms.

Starobinets *et al*[8,9] showed that stronger is the electrostatic interaction between the ion fixed and the opposite ion, the weaker is the carboxylate group attracted by the resin matrix and consequently the molecular adsorption is smaller. The order of the selectivity of the anions for the anion-exchange resin is[14]

$$NO_3^- < \text{carboxylate} < CrO_4^{2-} < SO_4^{2-}.$$

From the selectivity order, it is seen that SO_4^{2-} has the largest selectivity among other ions given here. So molecular adsorption is expected to be lowest in sulphate form of the resin. But from the results obtained as above, it is found that molecular adsorption is higher in sulphate and chromate forms than those in nitrate and carboxylate forms of the resin. So here the electrostatic interaction is not the main factor.

It has been already mentioned that, ion-exchange resin with multivalent counter-ions favours the adsorption of carboxylic acids by a mechanism involving site sharing[14]. So it may be expected that, inspite of electrostatic interactions, the acids are strongly held by the sulphate and chromate forms of the anion-exchange resin due to site sharing. It is also found that the order of adsorption by the two forms of the resin is $R_2SO_4 < R_2CrO_4$ for all the acids. The electrostatic interaction between the resin matrix and the counter-anion is higher for SO_4^{2-} ion than for CrO_4^{2-} ion. So here molecular adsorption is less in R_2SO_4 than in R_2CrO_4. The fact, that the molecular adsorption by carboxylate forms is larger by nitrate forms, is due to the presence of larger number of carbon atoms present in the anion-exchange resin and also due to formation of hydrogen bonding[11].

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Electrochemical Behaviour of Mixed Complexes of Cd(II) with Pyridine and γ-picoline at d.m.e.*

K. D. GUPTA, S. C. BAGHEL, K. K. CHOWDHARY and J. N. GAUR

Department of Chemistry, University of Rajasthan, Jaipur-302004

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Cathodic reduction of mixed cadmium-pyridine-γ-picoline complexes has been studied at the d.m.e. It has been found to be reversible and diffusion controlled involving two electron reduction. Three mixed complexes having stoichiometry 1 : 1 : 1, 1 : 1 : 2 and 1 : 2 : 1 are reported. The logarithm of overall formation constants β_{11}, β_{12} and β_{21} for the complexes [Cd(pyridine)(γ-picoline)]$^{2+}$, [Cd(pyridine)(γ-picoline$_2$)]$^{2+}$ and [Cd(pyridine)$_2$(γ-picoline)]$^{2+}$ are 2.11, 2.57 and 2 78 respectively. The tendency of complex (simple and mixed) to add and substitute another ligand is discussed.

PYRIDINE and γ-picoline[1] each forms 1:3 highest complexes with Cd(II). Mixed complexation was first of all studied by Schaap and McMasters[2] using polarographic measurements. The method of Schaap and McMasters has been applied by many others[3-7]. With Cd(II) three mixed complexes having stoichiometry 1:1:1, 1:2:1 and 1:1:2 are formed in solution.

Experimental

The solutions of $Cd(NO_3)_2$, KNO_3, pyridine and γ-picoline were prepared in double distilled water. Chemicals used were of reagent grade. The ionic strength was maintained constant at 1.0*M* using KNO_3 as the supporting electrolyte. The capillary of d.m.e. had the following characteristics m = 2 mg/sec., t=4.6 sec. at the height 66.5 cm of mercury head and the polarograms were obtained manually. The temperature was maintained constant at 30±1° throughout the experiment with the help of Hakke type ultra thermostat. The two fixed concentrations of pyridine used were 0.2*M* and 0.4*M*.

Results

Initially the complexes of Cd(II) with the ligands chosen were studied separately. The DeFord and Hume[8] method of graphical extrapolation was used to determine the overall formation constants of the consecutive simple complexes. The results are summarised below :

Complex		*Overall formation constant*
$[Cd(Py)]^{2+}$	β_{01}	20
$[Cd(Py)_2]^{2+}$	β_{02}	50
$[Cd(Py)_3]^{2+}$	β_{03}	65
$[Cd(\gamma-pic)]^{2+}$	β_{10}	60
$[Cd(\gamma-pic)_2]^{2+}$	β_{20}	300
$[Cd(\gamma-pic)_3]^{2+}$	β_{30}	440

TABLE 1—POLAROGRAPHIC MEASUREMENT AND Fij FUNCTIONS OF Cd(II)-γ-PICOLINE—PYRIDINE MIXED COMPLEXES AT 303°K.

$-E_{1/2}$ of simple metal ion = 0.6090 volts vs. SCE
i_d of simple metal ion = 69 div.
ionic strength = 1.0 *M*
[Pyridine] = 0.20 *M* fixed

C_X (γ-picoline) mole litre^{-1}	$-E_{1/2}$ Vs. S.C.E.	i_d (div.)	F_{00}	F_{10}	F_{20}	F_{30}
0.0	0.6090	69.0	—	—	—	—
0.1	0.6440	51.0	19.86	128.6	286	—
0.2	0.6554	48.0	47.23	201.1	505	425
0.3	0.6620	47.0	85.76	262.5	541	405
0.4	0 6685	47.0	141.30	335.7	589	423
0.5	0.6740	47.0	215.40	416.8	633	427
0.6	0.6785	46.0	310.90	506.5	677	429
0.7	0.6830	46.0	439.10	617.2	738	455

A = 7, B = 100, C = 420 and D_{av} = 425.

TABLE 2—POLAROGRAPHIC MEASUREMENT AND Fij FUNCTIONS OF Cd(II)-γ-PICOLINE-PYRIDINE MIXED COMPLEXES AT 303°K.

$-E_{1/2}$ of simple metal ion = 0.6090 volts vs. S.C.E.
i_d of simple metal ion = 69 div.
ionic strength = 1.0 *M*.
[Pyridine] = 0.40 *M* fixed.

C_X (γ-picoline) mole litre^{-1}	$-E_{1/2}$ Vs. S.C.E.	i_d (div)	F_{00}	F_{10}	F_{20}	F_{30}
0.0	0.6090	69	—	—	—	—
0.1	0.6535	49	42.85	228.5	585	450
0.2	0.6610	47	79.43	297.1	635	475
0.3	0.6675	47	130.80	369.3	664	414
0.4	0.6730	46	204.10	460.1	725	462
0.5	0.6775	44	301.00	562.0	784	488
0.6	0.6810	42	412.70	654.5	807	445
0.7	0.6850	42	561.00	772.8	861	458

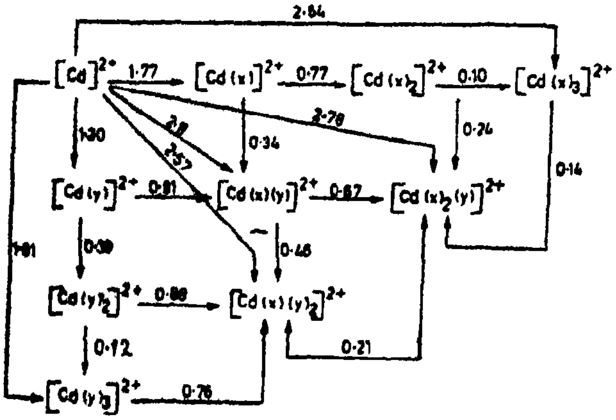
A = 20, B = 170, C = 540 and D_{av} = 450
β_{11} = 130, β_{12} = 375 and β_{21} = 600.

* Presented at the Annual Convention of Chemists, 1976 held at Bangalore.

The polarographic characteristics of mixed Cd(II)-pyridine and γ-picoline at fixed concentration of pyridine 0.2*M* and 0.4*M* are presented in Tables 1 and 2. From the two sets of A, B, C and D values β_{11}, β_{12} and β_{21} have been evaluated and are shown in Table 2.

Discussion

The equilibria among the various complexes present in solution is schematically shown below :



Scheme

In the above scheme the numerical values are the log K values where K is the equilibrium constants of the step indicated in the summary. From the above scheme following conclusions are drawn.

The equilibrium constant for the addition reaction of Y to $[Cd(Y)]^{2+}$ is less than the addition reaction of X to $[Cd(Y)]^{2+}$ which shows mixed complexation is favourable over the simple complex formation if a metal ion is present in the mixture of two ligands. The same may be concluded from the equilibrium constants of addition reactions of X to $[Cd(X)]^{2+}$ and Y to $[Cd(X)]^{2+}$, where X and Y stands for γ-picoline and pyridine concentration respectively.

X adds to $[Cd(Y)_2]^{2+}$ more easily than to $[Cd(X)_2]^{2+}$ and Y adds more easily to $[Cd(X)_2]^{2}$ than to $[Cd(X)_2]^{2+}$ (see summary). These facts also favour mixed complexation.

It is seen that $[Cd(X)_3]^{2+}$ can substitute Y and $[Cd(Y)_3]^{2+}$ can substitute X and $[Cd(X)(Y)_2]^{2+}$ can substitute X and not Y. The former statement supports mixed complexation and the latter one shows that X is a stronger ligand than Y.

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Infrared Spectral Studies of Calcium-Copper Hydroxylapatites

PREMA N. PATEL and S. V. CHIRANJEEVI RAO*

Post-Graduate Department of Chemistry, G. M. College, Sambalpur

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The introduction of Cu^{2+} in calcium hydroxylapatite results in the formation of its solid solutions. In the infrared spectral studies of the samples, the vibrations corresponding to ν_3 and ν_4 are shifted to lower frequencies due to an increase in mass and binding energy as a result of substitution of Ca^{2+} by Cu^{2+}.

CALCIUM hydroxylapatite which is also called bone mineral, $Ca_{10}(PO_4)_6(OH)_2$, (CaHA) is the major inorganic crystalline component of human skeletal system[1]. It undergoes a series of cationic and anionic replacement reactions[2]. $Ca^{2+} \rightarrow Cu^{2+}$ replacement reactions in CaHA is of extreme biological significance as it explains the mechanism of incorporation of copper into human skeletal system according to the following equation :

$$Ca_{10}(PO_4)_6(OH)_2 + nCu^{2+} \rightarrow Ca_{10-n}Cu_n(PO_4)_6(OH)_2 + n\,Ca^{2+}$$

As a part of a series of physicochemical investigations on calcium-copper hydroxylapatites the present work is an attempt at the infrared spectral studies of these compounds.

Experimental

The details of preparation and characterisation of the samples were reported earlier[3]. The samples used for infrared studies were acetone washed and air dried. The infra red tracings were carried on Perkin Elmer Instrument in KBr medium.

Results and Discussion

The results of chemical analyses by the method specially worked out[4] are given in Table 1. From the analytical data, the molecular formula of each of the sample was calculated and the molar gram atomic ratio of $\frac{Ca+Cu}{P}$ of each of the sample was found to have the value 1.67 (Theoretical 1.67). The infrared traces of the samples are given in Fig. 1. The calcium hydroxylapatite and its solid solutions with copper have hexagonal crystalline structure[5] and are interesting examples of solid state of fairly simple molecules of tetrahedral symmetry where bands become allowed due to relaxation of the molecular symmetry[6]. Tribasic phosphate ion in the free or undistorted state is tetrahedral—a member of Td point group. In this ideal symmetry only a few absorption bands corresponding to ν_4(570 cm^{-1}) and ν_3(1075 cm^{-1}) of PO_4^{3-} were clearly observed. From the spectra of the samples (Fig. 1) it could be seen that the ν_3 frequency corresponding to PO_4^{3-} ion are shifted to lower frequencies and the shape of the peaks was being affected by the introduction of Cu^{2+} into the crystalline lattice. The shift of ν_3 of PO_4^{3-} vibrations to lower frequencies may be due to the effect of binding energy and atomic mass. In Barnes' expression[7] $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$ which gives a relationship between frequency, atomic mass and force constant, the vibrational frequencies are dependent on the reduced mass μ of the participating atoms and the restoring force "K" between atoms, all other terms remaining constant. When the equilibrium distance between the positive and the negative atoms of the molecule is decreased, K generally increases in the above equation. Substitution of Ca^{2+} with a nucleus like Cu^{2+} gives rise to stronger coordination of the PO_4^{3-} group to the copper ion through oxygen. This in turn weakens the P O bond, lowering K (increasing P-O bond length) and the frequency is lowered. The PO_4^{3-} bending is normally around 520 cm^{-1} and bending modes do not shift very much under these conditions. But here the substitution is more complex, presumably because of the splitting of the triply degenerate mode at 600 cm^{-1} and thus there is an increase in the frequency from 520 cm^{-1} to 570 cm^{-1}. This theoretical explanation agrees well with the experimental data.

* For correspondence, present address : Chemist, Hinduthan Zinc Ltd., Visakhapatnam-15.

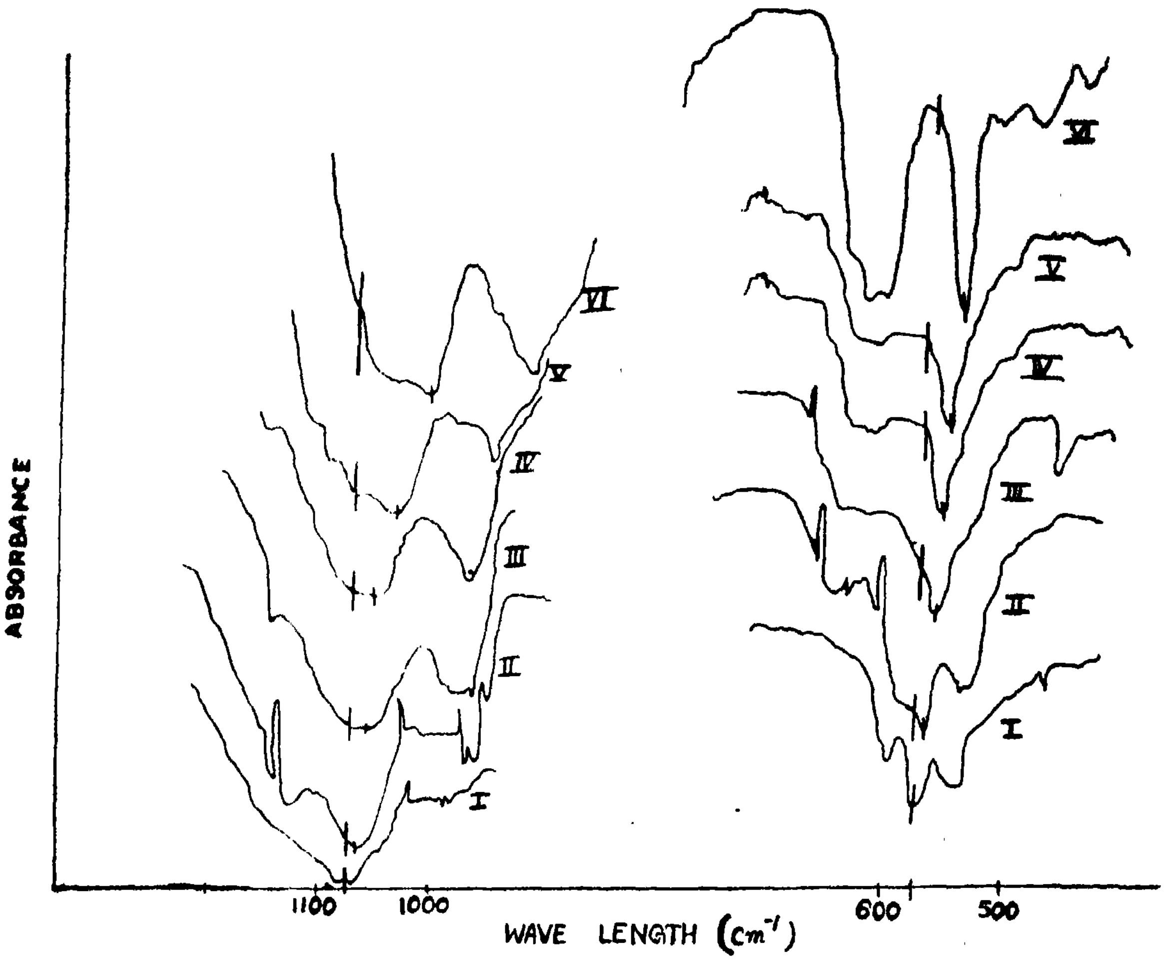


Fig. 1. Infrared Traces of Calcium-Copper Hydroxylapatites

TABLE 1 – CHEMICAL ANALYSES OF CALCIUM, COPPER HYDROXYLAPATITES AND THEIR SOLID SOLUTIONS

Sample No.	Wt % Ca	Cu	P	Molecular Formulae	g. atom ratio Ca+Cu/P
1	39.80	—	18.61	$Ca_{10}(PO_4)_6(OH)_2$	1.68
2	27.39	16.06	17.41	$Ca_{7.3}Cu_{2.7}(PO_4)_6(OH)_2$	1.67
3	21.48	23.66	16.89	$Ca_{5.9}Cu_{4.1}(PO_4)_6(OH)_2$	1.67
4	14.76	32.30	16.30	$Ca_{4.2}Cu_{5.8}(PO_4)_6(OH)_2$	1.67
5	6.02	43.52	15.53	$Ca_{1.8}Cu_{8.2}(PO_4)_6(OH)_2$	1.67
6	—	51.25	14.76	$Cu_{10}(PO_4)_6(OH)_2$	1.67

Acknowledgement

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Malate Complexes of Lanthanum(III) and Cerium(III)

NIRADA KUMARI MOHANTY and R. K. PATNAIK

Department of Chemistry, Regional Engg. College, Rourkela-769008, Orissa

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Lanthanum(III) and Cerium(III) form neutral complexes with malic acid below pH 6.4 and 6.1 respectively. The equilibrium constants of the reaction $M^{3+} + H_2ML \rightleftharpoons C + 3H^+$ are 3.75×10^{-11} and 1.67×10^{-10}, for lanthanum and cerium malate complexes respectively. The equilibrium constants of the reaction $M^{3+} + ML^{--} \rightleftharpoons C + H^+$ are 1.57×10^{-8} and 2.05×10^{-8} for lanthanum and cerium malates respectively.

MALATE complexes of rare earths were studied potentiometrically by Jercan and Popa[1]. Roulet *et al*[2] have also reported that malic, maleic and methyl succinic acids form 1:1 and 1:2 complexes with rare earths. This paper deals with the determination of the equilibrium constants on the formation of lanthanum and cerium malate complexes by pH metric method.

Experimental

pH titrations were carried out at $32 \pm 1°$ under nitrogen atmosphere with the help of a Marconi pH meter (TF 1093/1) having an accuracy of 0.02 pH. La and Ce were estimated gravimetrically as oxides after precipitation as oxalates and subsequent ignition. Ionic strength of 0.1 M was maintained by adding suitable amount of KNO_3 solution. Since the reactions were slow, the solutions were stored in stoppered bottles for 24 hours, before the measurements of pH.

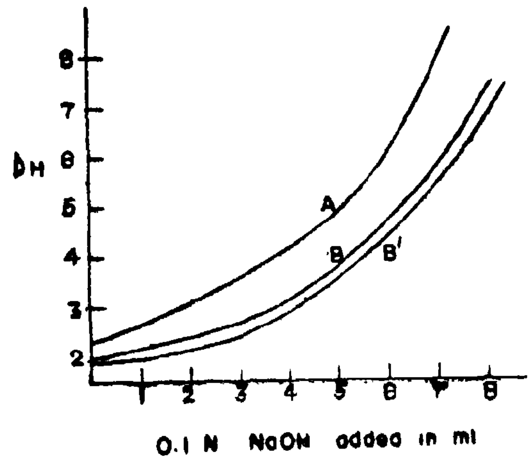


Fig. 1. pH titration of 50 ml of solution containing .003125 g. mole of malic acid and 0.005 g. mole of KNO_3 (curve A) and that of the same volume of two other solutions containing the same quantities of the above constituents and 0.00025 g. mole of lanthanum nitrate (curve B) and 0.00025 g. mole of cerium nitrate (curve B') against 0.1 N sodium hydroxide.

Results and Discussion

The proton liberation remains same when the metal to ligand ratio is increased from 1:1.25 to 1:5. This indicates the formation of a 1:1 type of complex in both cases of lanthanum and cerium.

The reaction in experiment 1 (Fig. 1) can be represented as

$$M^{3+} + H_3ML \rightleftharpoons C + nH^+ \quad (1)$$

It can be shown as in cases of citrate complexes of cadmium[3] and yttrium[4] and tartrate complex of yttrium[5] that,

$$\frac{\Delta[NaOH] - \frac{a}{b}\Delta[Ml]}{[C]} = n - a/b \quad (2)$$

when the formation of the complex is complete,

$$[C] = [La(NO_3)_3] \text{ or } [Ce(NO_3)_3]$$

The values of n at different pH were calculated. It was less than 3, below pH 6.4 and 6.1 in cases of lanthanum and cerium respectively. Hence a neutral complex is formed with liberation of 3 protons below these pH values. The equilibrium constants (K) of the reactions (1) are found to be 4.18×10^{-11}, 2.89×10^{-11}, 3.78×10^{-11}, 3.69×10^{-11} and 4.26×10^{-11} at pH 5.6, 5.8, 6.0, 6.1 and 6.4 respectively for lanthanum and 1.58×10^{-10}, 2.07×10^{-10}, 1.67×10^{-10} and 1.36×10^{-10} at pH 4.4, 5.0, 5.2 and 5.8 respectively for cerium. The mean values of K were 3.75×10^{-11} and 1.67×10^{-10} for lanthanum and cerium respectively.

In experiment 2 (Fig. 2), the pH of both the systems decreases gradually due to the liberation of protons during complex formation. The pH of both the systems are less than 5 indicating the formation of a neutral complex as observed in the previous experiment. The

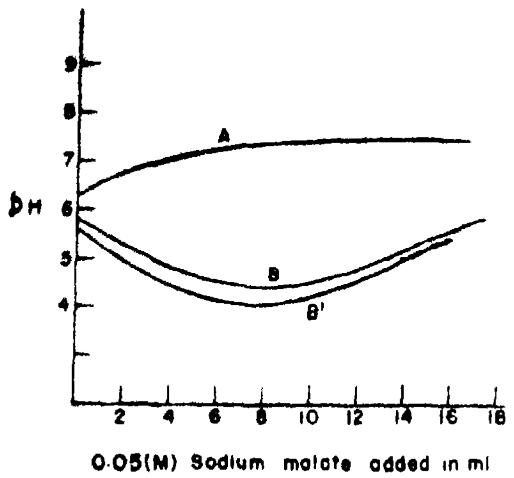


Fig. 2. *p*H titration of 50 ml of solution containing 0.005 g. mole of KNO_3 (curve A) and same volume of two other solutions containing the same quantities of the above constituents and 0 00025 g. mole of lanthanum nitrate (curve B) and 0 00025 g. mole of cerium nitrate (curve B') against 0.05 *M* sodium malate.

formation of this complex will be complete at about the 1:1 inflection point. The reaction in this experiment can be represented as

$$M^{3+} + ML \rightleftharpoons C + H^{+} \qquad (3)$$

$$K_3 = \frac{[C]\,[H^{+}]}{[M^{3+}]\,[ML^{--}]} \qquad (3-1)$$

Below the 1:1 equivalence point, it can be shown as in the tartrate complexes of manganese[6] and yttrium[5] and citrate complexes of cobalt[7] and yttrium[4] that

$$[M(NO_3)_3] = [C] + [M^{3+}]$$

$$[ML] = [C] + p[HML^{-}]$$

where $p = 1 + \frac{[H^{+}]}{k_1} + \frac{k_2}{[H^{+}]}$

$$[C] = [H^{+}] + r\,[HML^{-}]$$

where $r = 1 + 2\frac{[H^{+}]}{k_1}$

$$[HML^{-}] = \frac{[ML] - [H^{+}]}{r + p}$$

where [ML], $[HML^{-}]$, $[ML^{--}]$, [C] and $[M^{3+}]$ are represented by the molar concentrations of total malate, bimalate, malate complex and metal ion (lanthanum or cerium ions) respectively. k_1 and k_2 are the dissociation constants of malic acid[8] ($k_1 = 5.5\times10^{-4}$ and $k_2 = 2.1\times10^{-5}$)

K_3 values were calculated as before and are 1.27×10^{-3}, 2.21×10^{-3}, 1.43×10^{-3} and 1.39×10^{-3} at *p*H 5.0, 4.9, 4.8 and 4.7 respectively in case of lanthanum and 1.52×10^{-2}, 1.68×10^{-2}, 2.18×10^{-2} and 2.85×10^{-2} at *p*H 4.55, 4.5, 4.45 and 4.4 respectively in case of cerium system. The mean values are 1.57×10^{-3} and 2.05×10^{-2} for lanthanum and cerium respectively.

It can be shown that $K_3 \times k_1 \times k_2 = K$. The values of $K_3 \times k_1 \times k_2$ are 1.81×10^{-11} and 2.37×10^{-10} for lanthanum and cerium systems respectively which are exactly similar to the values of K obtained from experiment 1.

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Spectrophotometric Determination of Cerium(IV) with Triflupromazine Hydrochloride*

H. SANKE GOWDA and K. N. THIMMAIAH

Department of Post-graduate Studies and Research in Chemistry, University of Mysore, Manasa Gangotri, Mysore 570 006.

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Triflupromazine hydrochloride is proposed as a new reagent for the spectrophotometric determination of cerium(IV). The reagent forms red coloured species with cerium(IV) instantaneously in 2.5-4.0*M* phosphoric acid. The red species has absorption maximum at 503 nm with molar absorptivity 6.70 x 10^3 litre $mole^{-1}cm^{-1}$. A twenty-fold molar excess of the reagent is necessary for the full development of the colour intensity. Beer's law is valid over the concentration range 0.4-14.20 ppm of cerium(IV) The effects of acid concentration, time, temperature, order of addition of reagents, reagent concentration and diverse ions are reported. The proposed method offers the advantages of simplicity, selectivity, rapidity and without the need for extraction.

TRIFLUPROMAZINE hydrochloride(TPH), 10-[3 (dimethylamino)propyl]-2-trifluromethylphenothiazine hydrochloride was proposed as a spectrophotometric reagent for the determination of palladium[1] and gold[2]. The authors have now investigated the colour reaction between TPH and cerium(IV) and proposed TPH as a sensitive reagent for the spectrophotometric determination of cerium(IV).

Experimental

Apparatus : Beckman Model DB Spectrophotometer with stoppered silica cells of 1 cm optical path was used for absorbance measurements.

Reagents : Cerium(IV) sulphate solution : A stock solution of cerium(IV) sulphate was prepared in 0.5*M* sulphuric acid and standardised with arsenic(III) solution[3].

TPH solution : A 0.2% solution of TPH was prepared in doubly distilled water and stored in an amber bottle in a refrigerator.

Diverse ions : Solutions of diverse ions of suitable concentrations were prepared using analytical grade reagents.

Procedure recommended for the determination of cerium(IV) : Transfer the sample solution containing 10-355 μg of cerium(IV), 7.5 ml of 10*M* phosphoric acid and 3 ml of 0.2% TPH solution to a 25 ml volumetric flask and dilute to the mark with doubly distilled water. Mix the solution and measure the absorbance at 503 nm against a corresponding reagent blank prepared in the same manner. Calculate the cerium concentration of the sample solution by means of a calibration curve.

Results and Discussion

Determination of cerium(IV) : TPH is oxidised to red coloured species by cerium(IV) in sulphuric or phosphoric acid medium. The maximum colour development takes place instantaneously at room temperature (27°) in 2.5-4.0*M* phosphoric acid solutions (Table 1) as shown by the constancy of λ_{max}. The maximum colour intensity is not observed below 2.5*M* phosphoric acid. The reagent is slowly oxidised in phosphoric acid medium above 4.0*M*. The absorbance of the red coloured species assumed to be a radical cation remains constant for 35 min. The red colour is stable for about 5 min in sulphuric acid and unstable in hydrochloric acid. Nitric acid cannot be used as it oxidises TPH to a red coloured radical cation. Hence 3.0*M* phosphoric acid is conveniently chosen for all further work.

TABLE 1—EFFECT OF PHOSPHORIC ACID CONCENTRATION ON THE ABSORBANCE VALUES.

Amount of cerium(IV) taken = 4.5 μg/ml
λ_{max} = 503 nm.

Phosphoric acid *M*	Absorbance readings
1.00	0.1805
2.00	0.2007
2.50	0.2218
3.00	0.2218
3.50	0.2218
4.00	0.2218
4.50	0.2366
5.00	0.2596

* This paper was presented at the Annual Convention of Chemists, 1976 at Bangalore.

Absorption spectra. The absorption spectra of the red species and TPH are shown in Fig. 1. The phosphoric acid concentration in both the cases is $3M$. The maximum absorbance of the red species is found at 500-506 nm. The reagent under similar conditions does not absorb around this wavelength thus promoting excellent analytical conditions. The molar absorptivity is 6.70×10^3 litre $mole^{-1} cm^{-1}$ at the absorption maximum of 503 nm. According to Sandell's expression, the sensitivity of the reaction is 0.020 $\mu g/cm^2$.

excess of TPH is needed for completeness of the reaction. The absorbance is not affected by temperature in the range 7-50°. Above 50° the absorbance gradually decreases with the rise of temperature.

Calibration and range. Beer's law is obeyed from 0.5 to 14.2 ppm of cerium at wavelengths, 500, 503, 505 and 510 nm. The optimum range as evaluated by Ringbom's method is 1.2-13.70 ppm. The errors are in general about ± 2%.

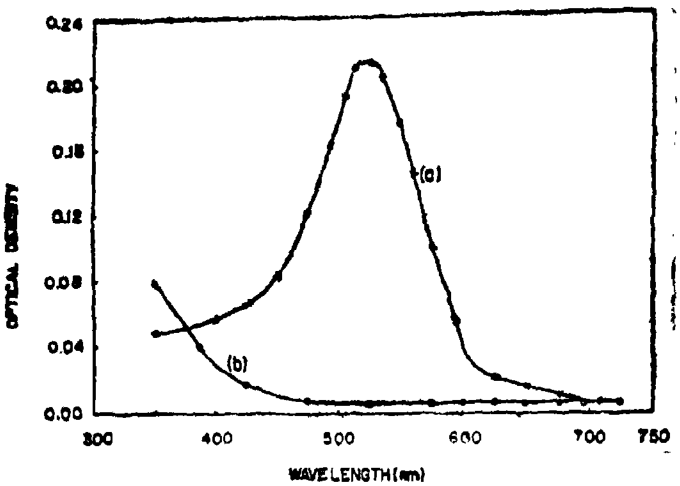


Fig. 1. Absorption spectrum of (a) red radical of TPH, (b) TPH. [TPH] = $6.5 \times 10^{-4} M$.

Order of addition of reagents. It was found that there was no appreciable change in the absorbance or in colour intensity of the red species if the order of addition of reagents was changed.

Effect of reagent concentration. The effect of reagent concentration was investigated by measuring the absorbance at 503 nm of solutions containing 4.5 ppm of cerium(IV) and varying the amount of reagent. The results are given in Table 2. A 20-fold molar

TABLE 2—EFFECT OF TPH CONCENTRATION ON THE ABSORBANCE VALUES

Amount of cerium(IV) taken = 4.5 μg/ml at 3.0M H_3PO_4 λ_{max} = 503 nm.

Molar excess of TPH	Absorbance readings
5.0	0.1871
10.0	0.2007
15.0	0.2147
20.0	0.2218
25.0	0.2218
30.0	0.2218
35.0	0.2218
40.0	0.2220
50.0	0.2220

Effect of diverse ions. In order to assess the possible analytical applications of the reaction, the effects of some ions which often accompany cerium were studied. For these studies different amounts of ionic species were added to 175 μg of cerium contained in 25 ml volumetric flask and the colour was developed as outlined in the procedure. The following amounts (μg/ml) of foreign ions were found to give less than 2% error in the determination of 7 μg/ml of cerium(IV), La(III) 4000, Pr(III) 4000, Nd(III) 4000, Gd(III) 4000, Dy(III) 4000, Ho(III) 4000, Er(III) 4000, Yb(III) ·000, Y(III) 4000, Tb(III) 4000, Os(VIII) 9, Ru(III) 6, Pd(II) 1.0, Pt(IV) 15, Ir(III) 10, Au(III) 0.3; Co(II) 290, Cu(II) 626.4, Ni(II) 571.7, Fe(III) 300, Ag(I) 12, Mg(II) 1500, Zn(II) 1619.2, Th(IV) 5.5, Zr(IV) 506, U(VI) 2100, As(V) 4000, chloride 8000, bromide 10400, iodide 0.16, fluoride 9086, sulphate 7600, acetate 6624, phosphate 7318, citrate 7200, tartrate 5342.9, nitrate 8000, thiosulphate 0.6 and EDTA 0.50.

It can be seen that many diverse cations especially lanthanides do not interfere in the determination of cerium(IV). The major advantage of this method is that TPH can be used as a selective reagent for the determination of cerium(IV) in presence of large quantities of other lanthanides in readily attainable oxidation states without the use of masking agents. The sensitivity of the proposed method is more than that of *o*-aminophenol[4], salicylhydroxamic acid[5] and

sulphanilic acid[8] which have been proposed as sensitive spectrophotometric reagents for cerium. The sensitivity of the present method is less than that of *o*-tolidine[7], diantipyrinyl-*p*-nitrophenyl methane[8], xylenol orange[9], *p*-aminoacetophenone[10] and phenyl anthranilic acid[11] which are used for the determination of cerium.

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Potentiometric Determination of Hydrazine or Lead Tetra acetate

M. R. MAHMOUD, M. S. EL-MELIGY and I. M. ISSA*

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt, A. R. E.

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Hydrazine is oxidized quantitively in acid solutions with lead IV acetate to yield nitrogen by the loss of 4-electrons. The factors affecting the success of potentiometric determination of hydrazine with lead IV acetate are investigated. As little as 0.13 mg of N_2H_4 per 50 ml of solution can be determined accurately in presence of 0.87*M* acetic acid. The reserve titration of lead IV acetate with N_2H_4 can be applied for the determination of lead tetraacetate. The reaction proceeds quantitatively within the concentration range 0.202-2.02 mg of Pb per 50 ml of solution. The titrations at the optimum conditions proceed fast and with adequate accuracy. The equivalent point in both cases is marked by a large potential jump.

LEAD IV acetate has been recently applied as an analytical reagent for the determination of many reducing agents including As^{3+}, Sb^{3+}, Sn^{2+}, Fe^{2+}, Cr^{3+}, Mo^{3+}, Tl^{1+} and Ru^{4+}.[1] The oxidation of N_2H_4 with Pb IV acetate has not been investigated, although different oxidizing agents have been applied for the determination of hydrazine depending upon its oxidation to nitrogen and water[2-7]. Recently Issa *et al.*[8] developed a method for the determination of N_2H_4 as low as 0.32 mg using potassium permanganate as oxidizing agent in presence of fluoride ions.

The present study deals with the reaction between Pb IV acetate and Hydrazine in order to device a method for the determination of macro- and micro-amounts of hydrazine or lead IV acetate.

Experimental

a) *Chemicals and Solutions* :

Lead IV acetate : The solid was prepared according to Braner[9] by heating Pb_3O_4 with a mixture of glacial acetic acid and acetic anhydride at 60°. The product was purified by recrystallization from acetic acid. ~0.05 *M* solution was then prepared by dissolving the appropriate weight of the solid in glacial acetic acid. The solution was then standardized potentiometrically against standard Fe II sulphate solution[10].

Hydrazine sulphate solution was prepared by dissolving the A.R. product in redistilled water. The reducing power of hydrazine was determined by recommended procedure[11]. Dilute solutions of hydrazine sulphate and lead IV acetate were prepared by quantitative successive dilution.

Other reagents were of analytical grade, twice distilled water and glacial acetic acid were used for the preparation of solutions and titration media.

*Deceased December, 1977

b) *Equipment* :

The e.m.f. of the titration cell was measured by a direct reading millivoltameter using a saturated calomel electrode as reference half-cell. A platinum electrode was used as indicator electrode which was always abraded with emery paper, etched with aqua regia and rinsed with water or glacial acetic acid before being used in each titration according to the medium in which the titration is performed.

On using hydrazine as titrant, the reference half-cell was connected to the titration cell with potassium chloride and Na-Ac acetic acid salt bridges.

c) *Working procedure* :

In the direct method appropriate volumes of solutions containing amounts of N_2H_4 ranging between 0.13-13.12 mg mixed with acetic acid to give an acidity of 0.174-8.70 *M* are titrated with leadIV acetate. In the reverse process different volumes of leadIV acetate containing 0.202-2.02 mg Pb in presence of acetic acid concentration >6.96 *M* are titrated with N_2H_4. The sudden change in the potential in both cases indicate the end point.

Results and Discussion

A) *Titration of Hydrazine by Lead Tetra Acetate* :

Effect of acetic acid concentration : Table 1, shows that good end points are obtained at acidities ranging between 0.174-8.70 *M* acetic acid. The titration curves obtained are more or less smooth and characterized by sharp inflections at the end points. The values of the formal redox potential of the N_2/N_2H_4 system depicted from the titration curves, indicate that the values shift slightly to more positive potential on increasing the acidities and hence hydrogen ions must be involved in the reaction of hydrazine with lead tetra acetate.

Acidity, *M* CH_3COOH 0.174,0.348,0.87,1.74,3.48,5.22,8.70
Redox potential of N_2/N_2H_4 couple, 0.310, 0.320, 0.33, 0.34, 0.35, 0.355, 0.365 Volt, Vs S.C.E.

TABLE 1—TITRATION OF 5ml 0.082 *N* N_2H_4 WITH 0.0972 *N* $Pb(AC)_4$ IN PRESENCE OF DIFFERENT AMOUNTS OF ACETIC ACID.

N, acetic acid	Theoretical end point, (ml)	Experimental end point, (ml)	Error %	Inflection at end point, mV/0.05 ml titrant
0.174	4.21	4.23	+0.12	280
0.348	4.21	4.22	+0.23	290
0.870	4.21	4.24	+0.71	270
1.74	4.21	4.24	+0.71	270
3.48	4.21	4.23	+0.47	290
5.22	4.21	4.24	+0.71	300
8.70	4.21	4.21	nil	240

Effect of hydrazine concentration: Amounts of hydrazine ranging between 0.13-13.12 mg can be determined with errors not exceeding 0.70%, on using the proper concentration of acetic acid (Table, 2.) The titration curves possess almost the same character irrespective of the concentration of N_2H_4 and are characterized by sharp inflections at the end point, which amount to 120 140 mV/0.05 ml of Pb IV acetate in dilute solutions. With larger amounts of hydrazine the end points are attained earlier than those expected, a fact which is readily attributed to the partial production of N_2H_2.

TABLE 2—RESULTS OBTAINED FOR THE POTENTIOMETRIC TITRATION OF HYDRAZINE WITH Pb IV ACETATE.

ml, N_2H_4	mg of N_2H_4	Theoretical end point ml	Experimental end point ml	Error %	Inflection at end point, mV/0.05 ml of titrant
Titration of 0.082 *N* N_2H_4 with 0.0976 *N* $Pb(AC)_4$					
2	1.30	1.685	1.70	+0.72	250
5	3.28	4.21	4.22	+0.24	290
10	6.56	8.42	8.44	+0.23	300
15	9.84	12.63	12.64	+0.08	320
20	13.12	16.84	16.78	−0.35	325
25	16.40	21.10	20.82	−1.32	325
45	29.52	37.89	36.95	−2.40	380
Titration of 0.0082 *N* N_2H_4 with 0.00976 *N* $Pb(AC)_4$					
2	0.13	1.685	1.68	−0.29	120
5	0.328	4.21	4.22	+0.24	130
10	0.656	8.42	8.38	−0.44	140

B) *Titration of lead IV acetate with hydrazine*:

Effect of acetic acid concentration: The data in Table 3 represent the titration of PbIV acetate with hydrazine at different acetic acid concentrations. The results indicate that the volume of hydrazine solution consumed in the titration is concordant with the theoretical one, corresponding to the oxidation of hydrazine to nitrogen and reduction of Pb^{4+} to Pb^{2+}. It is worthy to mention that the acetic acid concentration should exceed 6.96 *M*, otherwise Pb^{4+} may undergo hydrolysis to yield PbO_2. The titration curves are smooth and characterized by sharp inflections at the end point amounting on the average to 345-380 mV/0.05 ml of N_2H_4.

TABLE 3—TITRATION OF 5ml 0.0976 *N* $Pb(AC)_4$ WITH 0.082 *N* N_2H_4 IN PRESENCE OF DIFFERENT AMOUNTS OF ACETIC ACID.

Total normality	Theoretical end point (ml)	Experimental end point (ml)	Error (%)	Inflection at end point mV/0.05 ml of titrant
6.96	5.95	5.98	+0.50	360
8.70	5.95	5.98	+0.50	355
10.44	5.95	5.98	+0.50	345
13.90	5.95	6.00	+0.84	380

Effect of lead tetra acetate concentration: As is evident from the data included in Table 4, the titration of Pb IV acetate with N_2H_4 can be used as an analytical method for the determination of amounts as small as 0.202 mg of Pb IV. The titration curves are characterized by sharp inflection at the end point amounting to 500 mV/0.05 ml of N_2H_4.

TABLE 4—RESULTS OBTAINED FOR THE POTENTIOMETRIC TITRATION OF Pb IV ACETATE WITH HYDRAZINE.

ml of $Pb(AC)_4$	mg of $Pb(AC)_4$	mg of Pb	Theoretical end point (ml)	Experimental end point (ml)	Error (%)	Inflection at end point, mV/0.05ml of titrant
Titration of 0.0976 Pb IV acetate with 0.082 *N* N_2H_4						
2	43.40	20.20	2.38	2.40	+0.84	420
5	108.50	50.50	5.95	6.00	+0.84	430
10	217.00	101.00	11.90	12.00	+0.84	440
20	434.00	202.00	23.80	23.90	+0.42	490
30	651.00	303.00	35.82	36.85	+2.87	580
Titration of 0.00976 *N* $Pb(AC)_4$ with 0.0082 *N* N_2H_4						
2	4.34	2.02	2.38	2.38	Nil	220
6	13.02	6.06	7.14	7.08	−0.84	240
Titration of 0.000976 *N* $Pb(AC)_4$ with 0.00082 *N* N_2H_4						
2	0.434	0.202	2.38	2.36	−0.84	120
5	1.085	0.505	5.95	5.96	−0.16	140

From the quantities reacting at equivalence point at the optimum conditions, it is concluded that hydrazine is oxidized with PbIV acetate to nitrogen, where the reaction takes place can be considered to proceed according to the following equation:

$$2\,Pb(CH_3COO)_4 + N_2H_4 = N_2 + 2\,Pb(CH_3COO)_2 + 4\,CH_3COOH$$

This reaction is based on the two partial reactions :

$$N_2H_4 - 4\,e = N_2 + 4\,H^+$$

$$2\,Pb(CH_3COO)_4 + 4\,e + 4\,H^+ = 2\,Pb^{2+} + 4\,CH_3COO^- + 4\,CH_3COOH$$

From the results obtained, it is deduced that the oxidation of N_2H_4 with lead IV acetate is a quantitative reaction. This is supported by calculating the equilibrium constant and the degree of completion of the reaction. These are found to amount 6.92×10^{184} and 3.47×10^{22} respectively. These values were calculated from the potential of the systems involved viz. $E^\circ_{Pb\,IV/Pb\,II}$[12] $= 1.70$ V and $E^\circ_{N_2/N_2H_4} = -0.23$ V. However, on using the formal potential values, depicted from the titration curves, K and κ are found to amount to 3.35×10^{48} and 1.18×10^{8} respectively.

In addition, the method under hand involve an easy and accurate method for the micro- and macro-determination of Pb IV acetate where a few methods are known for this purpose[10,12].

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Synthesis of Isoxazolo (6,7-d) Benz (1,2) Isoxazoles and Furano (6,7-d) Benz (1,2) Isoxazoles.

K. A. THAKAR* and B. M. BHAWAL

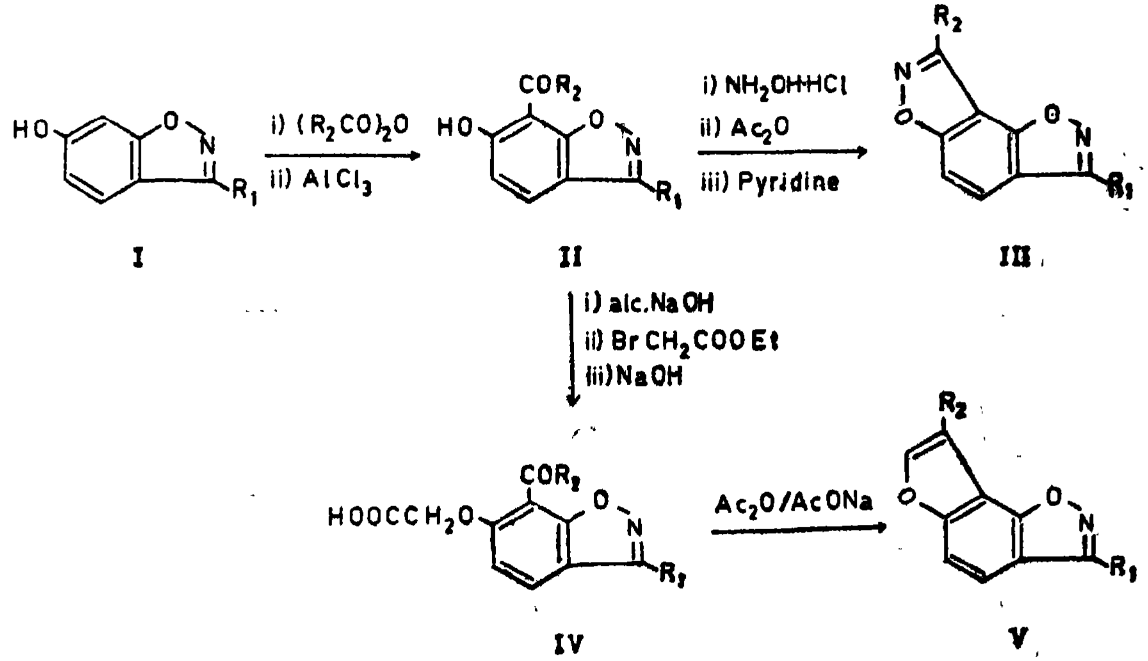
Department of Chemistry, Marathwada University, Auragabad 431004.

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Some isoxazolo (6, 7-d) benz (1,2) isoxazoles (III) and furano-(6,7-d) benz (1,2) isoxazoles (V) have been synthesised starting from 7-acyl-6-hydroxy benz (1,2) isoxazoles (II). These condensed heterocyclic ring systems in benz (1,2) isoxazole series are synthesized for the first time. The structures of starting materials, 7-acyl-6-hydroxy-benz (1,2) isoxazoles (II) have been confirmed by NMR spectral data. The antimicrobial activity of some of these comhounds has also been evaluated.

BENZ(1,2) isoxazoles are known to possess antifungal, antibacterial, antitubercular and analgesic properties[1-4]. A number of benzofurans are also known to possess antidepressive, diuretic and insecticidal properties[5-7]. It was, therefore, thought that these two moieties together may modify the physiological and biological properties. Moreover, these compounds represent new condensed heterocyclic ring systems.

The starting materials, 6-hydroxy-3-substituted benz(1,2)-isoxazoles (I, $R_1 = CH_3$ or CH_2CH_3) were obtained from resacetophenone and respropiophenone by a procedure reported by us earlier[8]. The esters of hydroxy-benz(1,2) isoxazoles were subjected to Fries migration[9] when 7-acyl-6-hydroxy-benz(1,2)isoxazoles(II) were obtained. The structures of these compounds(II) were confirmed by NMR spectral data (Table 1) which is discussed later. These *o*-hydroxy-acyl compounds(II) on treatment with hydroxylamine hydrochloride in presence of potassium hydroxide yielded oximes. The oximes were converted into their oxime acetates by acetic anhydride, which on refluxing with dry pyridine afforded isoxazolo (6,7-d) benz(1,2)isoxazoles(V).



SCHEME

The hydroxy-acyl benz(1,2) isoxazoles(II) were also converted into furano(6,7-d) benz(1,2) isoxazoles by Kostanecki and Tamber method[10].

The melting points, percentage yields, crystallisation solvents etc. of 6-hydroxy-7-acyl benz(1,2)isoxazoles(II),

*For correspondence.

TABLE 1—PHYSICAL AND NMR SPECTRAL DATA OF 6-HYDROXY-7-ACYL BENZ (1, 2) ISOXAZOLES (II)

Sr. No.	Compound II*		M.P. °C	Yield %	NMR spectral data (chemical shift in δ)						
					R_1		R_2		Aromatic protons		OH
	R_1	R_2			CH_2	CH_3	CH_2	CH_3	H^5	H^4	
1.**	CH_3	CH_3	122[a]	65	—	—	—	—	—	—	—
2.	CH_3	CH_2CH_3	88[b]	70	—	2.42 (s)	3.24 (q) J=7.5Hz	1.20 (t) J=7.5Hz	6.68 (d) J=8.5Hz	7.49 (d) J=8.5Hz	13.33 (s)
3.	CH_2CH_3	CH_3	72[b]	60	2.91 (q) J=7Hz	1.42 (t) J=7Hz	—	2.88 (s)	6.36 (d) J=8Hz	7.62 (d) J=8Hz	13.28 (s)
4.	CH_2CH_3	CH_2CH_3	65[a]	65	2.94 (q) J=7Hz	1.43 (t) J=7Hz	3.17 (q) J=7Hz	1.28 (t) J=7Hz	6.88 (d) J=8Hz	7.62 (d) J=8Hz	13.41 (s)

* Satisfactory analysis have been obtained for carbon and hydrogen.
** Reported earlier by S. S. Kumari et al.[8]
a : Crystallised from 60% alcohol ; b : Crystallised from 80% alcohol ;
s : singlet ; d : doublet ; t ; triplet ; q = quartet.

TABLE 2—PHYSICAL DATA OF INTERMEDIATE OXIMES, OXIME ACETATES AND ISOXAZOLO-(6,7-d) BENZ (1,2) ISOXAZOLES (III)

Sr. No.	Substituents		Intermediates				Isoxazolo (6,7-d)-benz (1,2) isoxazoles(III)*	
			Oximes		Oxime acetates			
	R_1	R_2	M.P. °C	Yield %	M.P. °C	Yield %	M. P. °C	Yield %
1.	CH_3	CH_3	214[a]	90	136[d]	75	157[d]	85
2.	CH_3	CH_2CH_3	184[b]	85	105[d]	70	94[c]	90
3.	CH_2CH_3	CH_3	170[b]	85	134[d]	70	98[c]	90
4.	CH_2CH_3	CH_2CH_3	146[b]	75	98[d]	65	78[c]	80

* Satisfactory analyses have been obtained for carbon and hydrogen.
a – crystallised from acetic acid ; b – crystallised from 60% alcohol ;
c – crystallised from 50% alcohol ; d – crystallised from alcohol.

TABLE 3—PHYSICAL DATA OF 7-ACYL-6-CARBETHOXY-METHOXY BENZ (1,2) ISOXAZOLES, 7-acyl-6-carboxy-methoxy BENZ (1,2) ISOXAOLES(IV) AND FURANO-(6,7-d) BENZ (1,2) ISOXAZOLE (V).

Sr. No.	Substituents		Carbethoxy-methoxy-benz (1,2) isoxazole*		Carboxy-methoxy-benz (1,2) isoxazole (IV)*		Furano-(6.7-d) benz (1,2)-isoxazole (V)*	
	R_1	R_2	M.P. °C	Yield %	M.P. °C	Yield %	M.P. °C	Yield %
1.	CH_3	CH_3	105[a]	75	208[b]	85	71[a]	65
2.	CH_3	CH_2CH_3	118[a]	70	198[a]	85	46[b]	60
3.	CH_2CH_3	CH_3	98[a]	80	174[a]	90	37[a]	60
4.	CH_2CH_3	CH_2CH_3	112[a]	70	178[a]	80	liquid**	50

* Satisfactory analyses have been obtained for carbon and hydrogen.
** Isolated as crude product due to insufficient quantity for further purification.
a — crystallised from 60% alcohol ; b – crystallised from 80% alcohol.

isoxazolo (6,7-d) benz(1,2) isoxazoles(III), furano(6,7-d) benz(1,2)-isoxazoles(V) and their corresponding intermediates are summarised in Tables 1, 2 and 3 respectively.

NMR spectra : The NMR spectra of 6-hydroxy-7-acyl benz(1,2) isoxazoles(II) were scanned on Varian 100 MHz instrument using TMS as an internal standard. The data is summarised in Table 1.

All hydroxy-acyl benz(1,2) isoxazoles(II) showed two doublets in the aromatic region for two ortho phenyl protons (J = 8Hz). This observation confirmed '7' position for the acyl group in these compounds. The down field (~13.3δ) OH proton indicated a strong hydrogen bonding.

Physiological activity : The antibacterial activity of some of these compounds has been evaluated using *M. tuberculosis and T. mentagrophytes*. 3-Ethyl-7-acetyl-6-hydroxy benz(1,2)isoxazole and 3-ethyl-3'-methyl isoxazolo (6,7-d) benz(1,2) isoxazole showed maximum activity in inhibiting the growth of *M. tuberculosis* at 100 ppm. The former compound is also found to be active against *T. mentagrophytes* at 200 ppm. In addition to this some compounds have been tested also against plant pathogens like, *Phoma herbarum*, *Helminthosporium apattarnae* and *Fusarium* sp. It was found that only 6-hydroxy-7-propionyl-3-methyl benz(1,2) isoxazole showed promising inhibition of growth of the above fungi at 50 ppm.

Experimental

All 6-hydroxy benz(1,2) isoxazoles(I) were prepared according to earlier reported procedures.

General procedures for the preparation of :

(i) *6-Hydroxy-7-acyl benz (1,2) isoxazoles(II)* : A mixture of hydroxy benz(1,2) isoxazole (0.1 mole), acid anhydride (0.12 mole) and pyridine (5 ml) was kept at room temperature for 4 hours and poured over crushed ice containing dilute hydrochloric acid. The acyloxy compound so obtained was crystallised from aqueous alcohol.

A mixture of the ester (0.05 mole) and anhydrous aluminium chloride (0.1 mole) was heated on an oil bath at 135-40° for about 2 hours. The resulting complex was decomposed with dilute hydrochloric acid and poured over crushed ice. The solid was dissolved in dilute sodium hydroxide solution and reprecipitated from the solution by acidification and crystallised from aqueous alcohol.

(ii) *Isoxazolo(6,7-d) benz(1,2) isoxazoles(III)* : A mixture of 6-hydroxy-7-acyl benz(1,2) isoxazole (0.01 mole), 40% potassium hydroxide solution (17 ml) and hydroxylamine hydrochloride (0.045 mole) was stirred, in an ice bath for about 4 hours. The cold, clear solution was neutralised with dilute hydrochloric acid. The resulting oxime was crystallised from aqueous alcohol.

The above oxime (1 g.) was warmed with acetic anhydride (2 ml) till it dissolved and kept at room temperature for 30 minutes and then poured over ice-water. The resulting oxime acetate was crystallised from alcohol.

The above oxime acetate (1g.) was refluxed with dry pyridine (10 ml) for about 3 hours. The resulting reaction mixture was poured on crushed ice containing enough dilute hydrochloric acid to neutralise pyridine. The solid obtained was filtered, washed with dilute sodium hydroxide solution and crystallised from aqueous alcohol.

(iii) *Furano (6,7-d) benz(1,2) isoxazole(V)* : A mixture of the sodium salt of hydroxy-acyl benz(1,2)-isoxazole (0.01 mole) and bromo acetic ester (0.11 mole) was heated on an oil bath at 130-40° for 2 hours. The reaction mixture was then poured on ice-water and the resulting carbethoxymethoxy compound was crystallised from aqueous alcohol.

The ester so obtained was heated with 1 *N* sodium hydroxide on a water bath for 30 minutes. The clear solution so obtained was neutralised with dilute hydrochloric acid. The resulting solid was crystallised from aqueous alcohol.

A mixture of the above phenoxy acetic acid (0.5 g), acetic anhydride (4 ml) and sodium acetate (1 gm) was refluxed on an oil bath at 160-70° for about 2 hours. The reaction mixture was then poured over ice. The resulting solid was washed with dilute sodium hydroxide and crystallised from aqueous alcohol.

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Heterocyclic Systems with Bridgehead Nitrogen Atom. Reactions of Cyclic Thioureas with α-Haloketones and Ketones in Presence of N.B.S.

VIJAY K. CHADHA

Department of Chemistry, Government Post Graduate College, Churu (Raj.)

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The reaction of *1H*-2-mercapto-4,5,6,7-tetrahydro [1,3] diazepine(II) with 2-bromo dimedone and indane-1,3-dione in presence of N-bromosuccinimide gave 8,8-dimethyl-2,3,4,5,7,8-hexahydro diazepino [2,1-b] benzothiazol-10 (9*H*)-one, (IV) and 2,3,4,5-tetrahydro indeno [1,2-d] thiazolo [3,2-a] [1,3] diazepine-11 (*H*)-one (V) respectively. Similarly II when condensed with α-heloketones yielded 3-substituted-5,6,7,8-tetrahydrothiazolo [3,2-a] [1,3] diazepines hydrohalides (VI). 2-Mercapto-3,4,5,6-tetrahydro pyrimidine(VII) on treatment with indane-1,3-dione in presence of NBS and α-heloketones furnished 2,3,4,5-tetrahydro indeno [1,2-d] thiazolo [3,2-a] pyrimidine-10(*H*)-one (VIII) and 3-substituted-4,5,6,7-tetrahydro thiazolo [3,2-a] pyrimidines (X) respectively. 3-substituted-5,6-dihydro-4*H*-imidazo [2,1-b] thiazoles (XII) were synthesized by reaction of 2-mercapto imidazoline (XI) with α-heloketones.

THE broad spectrum anthelmintic activity of (±)-6-phenyl-2,3,5,6-tetrahydro-4*H*-imidazo [2,1-b] thiazole hydrochloride (tetramisole hydrochloride)[1](I) against *Ascaris lubricoides* and *Enterobius vermicularis* in man[2] and against a variety of adult and immature gastrointestinal and pulmonary nematodes in laboratory animals, poultry and livestock[3] has been reported. In continuation to our earlier work on the synthesis of imidazo-thiazoles, thiazolo-pyrimidines, thiazolo diazepine, pyrimidino-benzothiazole[4] and thiazolo pyrimidine[5] some new tetramisole analogs have been reported in the present communication.

1H-2-Mercapto-4,5,6,7-tetrahydro [1,3] diazepine(II) when condensed with 2-bromo dimedone gave 8,8-dimethyl-2,3,4,5,7-8-hexahydro diazepino [2,1-b] benzothiazol-10 (9*H*)-one hydrobromide(III), which one neutralization with Sodium carbonate liberated the free base(IV). II on reaction with indane-1,3-dione in presence of N-bromo succinimide furnished 2,3,4,5-tetrahydroindeno [1,2-d] thiazolo [3,2-a] [1,3] diazepine-11 (*H*)-one(V), whereas with α-heloketones, 3-substituted-5,6,7,8-tetrahydro thiazolo [3,2-a] [1,3] diazepine hydrohelides were formed (See Chart).

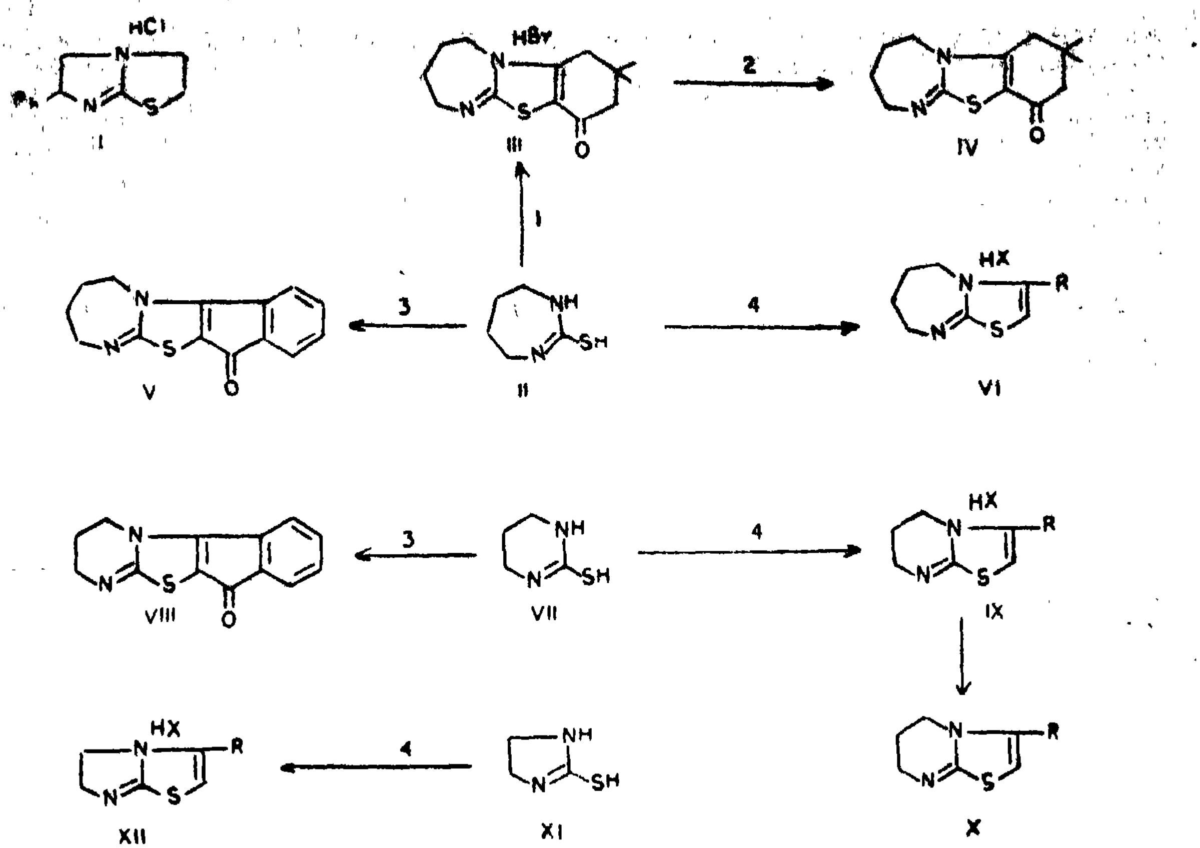
2,3,4,5-Tetrahydro indeno [1,2-d] thiazolo [3,2-a] pyrimidin-10 (*H*)-one(VIII) was synthesised by us[4] from condensation of 2-mercapto-3,4,5,6-tetrahydro-pyrimidine (VII) with indane-1,3-dione in presence of iodine. However the procedure is cumbersome and more time consuming (it requires about 30 hours of refluxing and then keeping the reaction mixture with ether for 48 hours). Hence N-bromo-succinimide has been used here in the synthesis of VIII. This considerably reduces the time period (about 6 hrs. of refluxing) and at the same time simplifies the work up. The yield is also comparable to that reported in the previous method. 3-substituted-4,5,6,7-tetrahydrothiazolo [3,2-a] pyrimidines(X) were synthesized by condensation of VII and α-heloketones and subsequent basification of the hydrohalide salt with sodium carbonate. 3-Substituted imidazo [2,1-b] thiazole(XII) were synthesised from 2-mercapto-imidazoline XI and α-heloketones following the Fefer and King's[6] method.

Structures III, IV, V, VI, X and XII have been characterised by IR spectra (vide experimental). Lack of absorption in the region 1670-1700 cm^{-1} in compounds VI, X and XII shows the absence of carbonyl group and suggesting the cyclic structure. The anthelmintic and antifungal testing is in progress and will be reported elsewhere.

Experimental

Melting points are uncorrected.

8,8-Dimethyl-2,3,4,5,7,8-hexahydro diazepino [2,1-b] benzothiazol-10 (9H)-one(IV) : A mixture of II (1.30 g, 0.01 mole) and 2-bromo dimedone (2.19 g, 0.01 mole) in anhydrous ethanol (30 ml) was heated under reflux on a steam bath for about 7 hours. The reaction mixture was concentrated and after cooling to room temperature, solid separated. It was recrystilized from ethanol in colourless needles m.p. 215°, yield 2.3 g (70%). (Found : S, 9 38 ; N, 8.27 ; Calcd. for $C_{13}H_{19}N_2SO$ Br. S, 9.67 ; N, 8.46%). ν_{max}^{KBr} (cm^{-1}) 1361, 1389 (gem dimethyl), 1449 (C-H deformation in CH_2), 1550, 1608, (C=C, C=N), 1695 (C=O), 2941 (C-H stretching in CH_2), 3125 ($\overset{+}{N}H$).



1. 2-Bromo Dimedone, EtOH ; 2. Na_2CO_3 ; 3. Indane-1,3-Dione, NBS ; R $COCH_2X$, EtOH.

The above hydrobromide (1.0 g) was dissolved in boiling water and neutralized with Sodium carbonate solution to give the free base m.p., 162° (Found : S, 12.49 ; N, 10.91 ; Calcd. for $C_{18}H_{18}N_2SO$; S, 12.80 ; N, 11.20%) ν_{max}^{Nujol} (cm^{-1}) 1570, 1620 (C=C, C=N), 1670 (C=O).

2,3,4,5-Tetrahydro indeno [1,2-d] thiazolo [3,2-a] [1,3] diazepine-11 (H)-*one* (*V*) : A mixture of indane-1,3-dione (1.46 g, 0.01 mole) N-bromosuccinimide (1.78 g, 0.01 mole) in Carbon-tetrachloride (30 ml) was refluxed for about 2 hours. The reaction mixture was filtered and the solvent distilled off. The residue was further refluxed with II (1.30 g) in anhydrous ethanol for about six hours. The dark green coloured solid was filtered and washed with ethanol. m.p. 172°, yield 4[illegible]%. (Found : S, 12.24 : N, 10.67, Calcd. for $C_{14}H_{12}N_2SO$: S, 12.50 ; N, 10.94%). ν_{max}^{Nujol} (cm^{-1}), 1455 (C-N stretching) 1585, 1610 (C=C, C=N), 1710 (C=O).

3-m-*Nitrophenyl-5,6,7,8-tetrahydro-thiazolo [3,2-a] [1,3] diazepine hydrobromide* (*VI, R*=m-NO_2-C_6H_4, *X*=*Br*) : Compound II (1.30 g, 0.01 mole), *m*-nitrophenacyl bromide (2.44 g, 0.01 mole) and anhydrous ethanol (30 ml) was heated under reflux on a steam bath for 7-8 hours. The solvent was distilled off and the residue crystallised from ethanol, m.p. 190° (decomp). Yield 2.7 g (73%). (Found : S, 8.63 ; N, 11.44 : Calcd. for $C_{13}H_{14}N_3SO_2$ Br. S, 8.99 ; N, 11.80%). ν_{max}^{Nujol} (cm^{-1}), 730,810,1580,1620 (C=C, C=N), 3100 ($\overset{+}{N}$H).

Other thiazolo-diazepines were prepared similarly. VI (R=*m*-NO_2-C_6H_4), m.p. 135-37°. Yield 81% (Found : S, 11.27 ; N, 14.94 ; Calcd. for $C_{13}H_{13}N_3$-SO_2 : S, 11.63 : N, 15.27%). VI (R=*p*-Cl-C_6H_4), 13[illegible]°, 62% (Found : S, 11.84 : N, 10.22 ; Calcd. for $C_{13}H_{13}N_2SCl$: S, 12.10 : N, 10.59%). VI (R=2-Benzothiazolyl, X=Br), 205° (decomp.), 77%. (Found : S, 17.04 : N, 11.05 ; Calcd. for $C_{14}H_{14}N_3S_2$ Br : S, 17.39 : N, 11.41%). VI(R=C_6H_5, X=Cl), 170° (decomp), 85%. (Found : S, 11.68 : N, 10.19 ; Calcd. for $C_{13}H_{15}N_2SCl$: S, 12.00 : N, 10.51%).

2,3,4,5-Tetrahydro indeno [1,2-d] thiazolo [3,2-a] Pyrimidin-10 (H)-*one* (*VIII*) : Indane-1,3-dione (1.46 g, 0.01 mole), N-bromosuccinimide (1.[illegible]8 g, 0.01 mole) in carbon-tetrachloride (20 ml) was refluxed for about one and a half hour. The reaction mixture was filtered and the solvent was distilled off. The residue was refluxed

with VII[8] (1.16 g, 0.01 mole) in anhydrous ethanol (30 ml) for about 6 hours. The solid which separated at the end of the refluxing period was filtered, dissolved in boiling water and purified (charcoal). Neutralization with Sodium carbonate solution gave yellow coloured solid m.p. 212° (decomp) (ethanol) yield 1.45g (59%). Mixture melting point with the sample[4] remained undepressed. (Found : S, 12.87 : Calcd. for $C_{13}H_{10}N_2SO$: S, 13.22%).

3-m-Nitrophenyl-4,5,6,7-tetrahydro thiazolo [3,2 a] Pyrimidin (X,R = m-NO_2-C_6H_4) : It was synthesised by treating VII (1.16 g, 0.01 mole) and *m*-nitrophenacyl bromide (2.44 g, 0.01 mole) in anhydrous ethanol (30 ml) as in the case of VI. Hydrobromide salt m.p 217°. Yield 3.2 g (93%). (Found : S, 8.89 : N, 11.92. Calcd. for $C_{12}H_{12}N_3SO_2Br$: S, 9.35 : N 12.29%). The hydrobromide salt (1.0 g) was dissolved in boiling water and on treatment with sodium carbonate yielded the free base m.p. 165° (decomp.) (Found : S, 12.04 : N, 15.61 : calcd. for $C_{12}H_{11}N_3SO_2$, S, 12.26 : N, 16.09%) ν_{max}^{Nujol} (cm^{-1}) 710, 810, 1590, 1620 (C=C, C=N).

Other thiazolo-pyrimidines were prepared in a similar way. IX (R=*p*-H_3CO-C_6H_4, X=Br), m.p. 230° (decomp.) Yield 55%. (Found : S, 9.33 : N, 8.41 : Calcd. for $C_{13}H_{15}N_2SO$ Br : S, 9.78 : N, 8.56%). IX (R=2-Benzothiazolyl, X=Br), 257° (decomp.), 87%. (Found : S, 17.76 : N, 11.66 : Calcd. for $C_{13}H_{12}N_3S_2$, Br: S, 18.08 : N, 11.87%). IX. (R=C_6H_5, X=Cl), 202°, 83%. (Found : S, 12.31 : N, 10.83 : Calcd. for $C_{12}H_{13}N_2$ SCl : S, 12.67 : N, 11.09%).

3-m-Nitrophenyl-5, 6-dihydro-4H-imidazo [2, 1-b] thiazole (XII, R = m-NO_2-C_6H_4) : It was prepared as described above by reacting XI[8] (1.02 g, 0.01 mole), *m*-nitrophenacyl bromide (2.44 g, 0.01 mole) in anhydrous ethanol (30ml). Hydrobromide salt m.p. 275° (decomp). Yield 2.7 g.(82%) (Found : S, 9.38, N,12.59 : Calcd. for $C_{11}H_{10}N_3SO_2Br$ S, 9.75 ; N, 12.80%). The salt on treatment with sodium carbonate liberated the free base, m.p. 168-70° (decomp). Yield 90% (Found : S, 12.48 : N, 16.57, Calcd. for $C_{11}H_9N_3SO_2$, S, 12.95 : N, 17.00%). ν_{max}^{Nujol} (cm^{-1}) 690, 790, 1520, 1550, 1610 (C=C, C=N).

Similarly other imidazo-thiazoles were synthesized. XII (R=3,4 $(HO)_2$ C_6H_3, X=Cl), m.p. 235-37°, Yield 94%. (Found : S, 11.61 : N, 10.23 : Calcd. for $C_{11}H_{11}N_2SO_2Cl$: S, 11.82 ; N, 10.35%). XII (R=2, 3, 4 $(HO)_3C_6H_2$, X=Cl), 222° (decomp.), 59%. (Found : S, 10.93 : N, 9.39 : Calcd. for $C_{11}H_{11}N_2SO_3Cl$: S, 11.18 : N, 9.76%) : XII (R=*p*-H_3CO-C_6H_4, X=Br), 230°, 54% (Found : S, 10.07. N, 8.44 : Calcd. for $C_{12}H_{13}N_2SO$ Br. : S, 10.22, N, 8.95%). XII. (R=C_6H_5, X=Cl), 215°, 65% (Found : S, 13.11 ; N, 11.29 : Calcd for $C_{11}H_{11}N_2SCl$: S, 13.42 ; N, 11.74%)

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Studies on 2-*N*-Isobutyl/Isopropyl Carboxamidomethyl Thio-3-Aryl-4 (3H) Quinazolinones

P. N. BHARGAVA and SHREE PRAKASH

Department of Chemistry, Banaras Hindu University, Varanasi-221005, India

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2-*N*-Isobutyl/isopropyl Carboxamidomethyl thio-3-aryl-4 (3H) quinazolinones have been synthesised by the reaction of 2-mercapto-3-aryl-4 (3H) quinazolinones and *N*-isobutyl (or isopropyl)-2-chloroacetamide in ethanol at room temperature.

DURING the last two decades, a number of quinazolinones and their derivatives have been screened for their remarkable biological and pharmacological activities such as antimalarial[1,2], antibacterial[3], ataractic[4], diuretic[5], hypnotic[6] and anticonvulsant[7,8] The anticonvulsant property of 2-methyl-3-*o*-tolyl-4(3H)-quinazolinone[9] has been reported in mice, rats and dogs. Hypothermic activity in rats and antipyretic activity in rabbits[10] of 2-methyl-3-aryl-4(3H)-quinazolinones have also been reported.

The above observations led Bhargava *et al*[11,12] to prepare S-substituted-2-mercapto-3-aryl-4(3H)-quinazolinones as possible antitubercular[11] and antimalarial[12]. In the present communication, the syntheses of 2-*N*-isobutyl (or isopropyl)-carboxamidomethylthio-3-aryl-4(3H) quinazolinones from anthranilic acid, aryl isothiocyanates and *N*-isobutyl (or isopropyl)-2-chloroacetamide[13] have been reported.

Experimental

Melting point of the compounds were recorded on Gallencamp apparatus and are uncorrected. A Varian A60D, a Perkin Elmer 257 and a Coleman analyser were used for NMR, IR and elemental analysis respectively.

2-Mercapto-3-aryl-4(3H)-quinazolinones : These were prepared by the method of Bhargava and Ram[14].

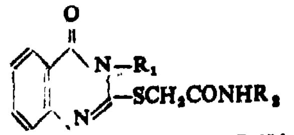
2-(N-Isobutylcarboxamidomethylthio)-3-phenyl-4-(3H) quinazolinone : 2–Mercapto-3-phenyl-4(3H) quinazolinone (3.2 g) was dissolved in minimum amount of 10% alc. sodium hydroxide. To this was added 1.4 ml of *N*-isobutyl-2-chloroacetamide with constant stirring for an hour at room temp. It was left overnight and a crystalline solid obtained was filtered and washed. Recrystallisation from ethanol afforded white shinning crystals, yield 73%, m.p. 150°. TLC: $R_f = 0.32$ (benzene-ether, 3 : 1). Anal. Calcd. for $C_{20}H_{21}N_3O_2S$: C, 65.39 ; H, 5.72 ; N, 11.44 ; S, 8.71. Found: C, 65.03 ; H, 5.94 ; N, 11.81 ; S, 9.22%. IR, ν_{max}^{nujol} : 3300 (m, N H), 16 7(s), 1648(s), 1612(w), 1580(w), 1555(s) cm^{-1} ; NMR ($CDCl_3$) δ : 8.27(1H, m), 6.9-7.8 (9H, m), 3.79(2H, s), 3.07 (2H, dd, $J = 7, 6$ Hz), 1.72(1H, m), 0.84(6H, d, $J = 6$ Hz).

Other S-substituted quinazolinones were prepared similarly. Their physical constants are recorded in Tables 1 and 2.

2-(N-Isopropyl carboxamidomethylthio)-3-aryl-4-(3H)-quinazolinones : These were prepared (Table 1) in a similar manner as described above using *N*-isopropyl 2-chloroacetamide. IR and NMR data are recorded in Table 3.

Microbial activity : Some of the compounds of Table 1 (IIb, IIe, IIg and IIh) were tested for antibacterial activity against *S. aureus*, *S. typhi*, *E. coli* and *A. tumefaciens* ; for antifungal activity against *C. albicans*, *C. neoformans*, *M. canis* and *A. niger* at a maximum tested concentration of 100 μg/ml and the compounds IIg and IIh were screened for their antitubercular activity against *M. tuberculosis* H37Ra in Lowenstein-Jensen's medium at a concentration upto 100μg/ml. But none of them showed any significant activity.

TABLE 1



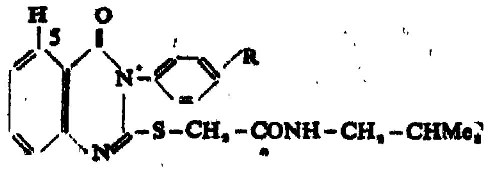
I, $R_2 = C_4H_9$ (iso); II, $R_2 = C_3H_7$ (iso)

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF S-SUBSTITUTED-2-MERCAPTO-3-ARYL-4 (3H)-QUINAZOLINONES.

Comp. No.	R_1	Mol. formula	Yield (%)	M.P (°C)	C%		H%		N%		*R_f values
					Found	Calcd.	Found	Calcd.	Found	Calcd.	
Ia	*o*-Tolyl	$C_{21}H_{23}N_3O_2S$	69	145	65.83	66.14	6.52	6.04	11.32	11.02	0.37
Ib	*m*-Tolyl	$C_{21}H_{23}N_3O_2S$	92	181	66.43	66.14	6.74	6.04	11.45	11.02	0.37
Ic	*p*-Tolyl	$C_{21}H_{23}N_3O_2S$	75	177	66.01	66.14	6.19	6.04	10.85	11.02	0.33
Id	*p*-Chlorophenyl	$C_{20}H_{20}N_3O_2SCl$	82	195	59.21	59.77	5.57	4.98	10.38	10.45	0.36
Ie	*p*-Methoxyphenyl	$C_{21}H_{23}N_3O_3S$	71	183	63.69	63.47	5.79	5.79	10.48	10.57	0.26
If	*p*-Ethoxyphenyl	$C_{22}H_{25}N_3O_3S$	64	204	64.38	64.23	6.35	6.08	10.46	10.21	0.32
IIa	Phenyl	$C_{19}H_{19}N_3O_2S$	65	193	64.82	64.50	5.54	5.38	12.23	11.89	0.36
IIb	*o*-Tolyl	$C_{20}H_{21}N_3O_2S$	76	169	64.94	65.38	5.81	5.72	11.74	11.40	0.42
IIc	*m*-Tolyl	$C_{20}H_{21}N_3O_2S$	68	210	65.60	65.38	5.99	5.72	11.12	11.40	0.42
IId	*p*-Tolyl	$C_{20}H_{21}N_3O_2S$	82	188	65.91	65.38	5.08	5.72	12.00	11.40	0.38
IIe	*p*-Chlorophenyl	$C_{19}H_{18}N_3O_2SCl$	63	216	59.43	58.81	4.87	4.64	10.26	10.83	0.37
IIf	*p*-Methoxyphenyl	$C_{20}H_{21}N_3O_3S$	74	204	62.24	62.64	5.71	5.48	10.82	10.96	0.28
IIg	*p*-Ethoxyphenyl	$C_{21}H_{23}N_3O_3S$	71	271	63.62	63.42	5.20	5.79	10.44	10.58	0.33
IIh	Benzyl	$C_{20}H_{21}N_3O_2S$	84	211	65.14	65.38	5.68	5.72	11.05	11.40	0.32

*R_f values were measured on developing the TLC plates (adsorbent, silica gel B. D. H.) in Benzene-Ether (3 : 1) mixture.

TABLE 2

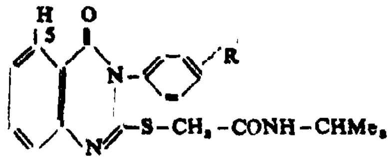


NMR* AND IR SPECTRAL DATA OF I

Comp. No.	R	δ(ppm)							ν (cm⁻¹)	
		H-5	Other aromatic protons & -NH-	S-CH_2	NH-CH_2-	-*CH*-	Me_2	R	Characteristic IR peaks	
Ia	*o*-Methyl	8.25 (1H, m)	6.73–7.96 (8H, m)	3.78 (2H, s)	3.09 (2H, dd, *J*=6,7 Hz)	1.72 (1H, m)	0.81 (6H, d, *J*=6 Hz)	2.13 (3H, s)	3287 (m), 1658 (s), 1578 (w),	1685 (s) 1615 (w) 1558 (s).
Ib	*m*-Methyl	8.28 (1H, m)	6.90–7.83 (8H, m)	3.78 (2H, s)	3.08 (2H, dd, *J*=6,7 Hz)	1.74 (1H, m)	0.83 (6H, d, *J*=6 Hz)	2.42 (3H, s)	3300 (m), 1648 (s), 1582 (w),	1698 (s) 1616 (w) 1558 (s).
Ic	*p*-Methyl	8.30 (1H, m)	6.78–7.95 (8H, m)	3.81 (2H, s)	3.10 (2H, dd, *J*=6,7 Hz)	1.81 (1H, m)	0.83 (6H, d, *J*=6 Hz)	2.45 (3H, s)	3290 (m), 1662 (s), 1583 (w),	1692 (s) 1618 (w) 1560 (s).
Id	*p*-Chloro	8.26 (1H, m)	6.85–7.93 (8H, m)	3.80 (2H, s)	3.08 (2H, dd, *J*=6,7 Hz)	1.78 (1H, m)	0.82 (6H, d, *J*=6 Hz)	—	3310 (m), 1648 (s), 1578 (w),	1695 (s) 1610 (w) 1550 (s).
Ie	*p*-Methoxy	8.28 (1H, m)	6.72–7.88 (8H, m)	3.79 (2H, s)	3.09 (2H, dd, *J*=6,7 Hz)	1.73 (1H, m)	0.83 (6H, d, *J*=6 Hz)	3.89 (3H, s)	3315 (m), 1650 (s), 1578 (w),	1700 (s) 1620 (w) 1554 (s).
If	*p*-Ethoxy	8.27 (1H, m)	6.76–7.94 (8H, m)	3.80 (2H, s)	3.10 (2H, dd, *J*=6,7 Hz)	1.75 (1H, m)	0.84 (6H, d, *J*=6 Hz)	1.41 (3H, t, *J*=7 Hz) 4.14 (2H, q, *J*=7 Hz)	3305 (m), 1652 (s), 1580 (w),	1695 (s) 1614 (w) 1548 (s).

*NMR spectra were recorded in $CDCl_3$ using TMS as internal standard at 44°. Total number of protons and multiplicity of bands are indicated in parenthesis.

TABLE 3



NMR* AND IR SPECTRAL DATA OF II

Comp. No.	R	δ (ppm) H-5	Other aromatic protons & -NH-	S-CH_2-	NH-CH-	Me_2	R	ν (cm^{-1}) Characteristic IR peaks		
IIa	H	8.30 (1H, m)	6.78 – 7.95 (9H, m)	3.73 (2H, s)	4.00 (1H, m)	1.10 (6H, d, J=6 Hz)	—	3300 (m), 1615 (w),	1697 (s), 1582 (w),	1648 (s) 1553 (s).
IIb	o-Methyl	8.29 (1H, m)	6.80 – 8.02 (8H, m)	3.73 (2H, s)	3.99 (1H, m)	1.08 (6H, d, J=6 Hz)	2.15 (3H, s)	3275 (m), 1615 (w),	1686 (s), 1580 (w),	1650 (s) 1556 (s).
IIc	m-Methyl	8.30 (1H, m)	6.66 – 7.88 (8H, m)	3.72 (2H, s)	3.99 (1H, m)	1.10 (6H, d, J=6 Hz)	2.40 (3H, s)	3290 (m), 1617 (w),	1698 (s), 1583 (w),	1645 (s) 1556 (s).
IId	p-Methyl	8.28 (1H, m)	6.88 – 7.74 (8H, m)	3.73 (2H, s)	4.00 (1H, m)	1.10 (6H, d, 7=6 Hz)	2.42 (3H, s)	3295 (m), 1615 (w),	1700 (s), 1582 (w),	1643 (s) 1558 (s).
IIe	p-Chloro	8.25 (1H, m)	6.82 – 7.84 (8H, m)	3.74 (2H, s)	3.94 (1H, m)	1.09 (6H, d, . =6 Hz)	—	3300 (m), 1616 (w),	1700 (s), 1582 (w),	1641 (s) 1558 (s).
IIf	p-Methoxy	8.23 (1H, m)	6.79 – 7.80 (8H, m)	3.71 (2H, s)	3.95 (1H, m)	1.10 (6H, d, J=6 Hz)	3.86 (3H, s)	3320 (m), 1618 (w),	1692 (s), 1583 (w),	1647 (s) 1560 (s).
IIg	p-Ethoxy	8.23 (1H, m)	6.85 – 7.82 (8H, m)	3.71 (2H, s)	3.93 (1H, m)	1.10 (6H, d, J=6 Hz)	1.40 (3H, t, J=7 Hz) 4.11 (2H, q, J=7 Hz)	3295 (m), 1617 (w),	1690 (s), 1581 (w),	1662 (s) 1559 (s).

*NMR spectra were recorded in $CDCl_3$ using TMS as internal standard at 44°. Total number of protons and multiplicity of bands are indicated in parenthesis.

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Kinetics of Base Catalysed Iodination of Acetophenones

N. SATYANARAYANA and E. V. SUNDARAM

Department of Chemistry, P. G. Centre, Warangal–506009, India

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The kinetics of iodination of acetophenone and its derivatives has been studied in various carboxylate buffers in 50% $MeOH-H_2O$ v/v. The reaction was found to be first order in acetophenone and catalyst, and zero order in iodine. The activation parameters like $\Delta E^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were evaluated. The Hammett reaction constants 'ρ' were evaluated for different acids. The ionisation constants of different acids like propionic, acetic, lactic, glycollic and chloroacetic were determined experimentally in 50% $MeOH-H_2O$ v/v at 35°. The catalytic constants in different buffers were measured at 35° for each acetophenone in 50% $MeOH-H_2O$ The Bronsted coefficients 'β' were evaluated for each acetophenone and correlated with reaction constant 'ρ'.

EVEN though a detailed study on the halogenation of aliphatic and cyclic ketones was done by many workers[1-3], not much work seems to have been done on the halogenation of ketones using general base catalysis. A recent publication by Mhala et al[4]. has prompted us to publish our results.

In this communication we are presenting the work on iodination of acetophenone and substituted acetophenones in 50% MeOH with various carboxylate anions as catalysts with an aim to find the catalytic constants and also to correlate the reaction constant 'ρ' with Bronsted coefficient 'β'.

Experimental

All the chemicals used were of AnalaR grade. Acetophenones were purified by known methods and the E-Merck quality methanol was distilled before use. An Elico *p*H-meter model L_1-10 was used for determining ionisation constants of the acids.

The reaction rate constants were measured in buffer solutions, prepared from NaOH (free from carbonate) and various carboxylic acid solutions in 50% $MeOH-H_2O$. The stock solutions of acetophenones in pure methanol and iodine in aqueous KI were prepared. The concentrations of acetophenone and I_2 were 0.05*M* and 0.005*M* respectively with varying buffer concentrations in the reaction mixture and the reaction was studied at a constant ionic strength ($\mu = 0.6M$). The reaction at different temperatures (30-45°) with acetate buffer and at 35° with other buffers was followed by pipetting out aliquot portions of the reaction mixture into ice-cold water and excess iodine was titrated with standard thiosulfate. In all the cases pseudo-first order rate constants were calculated by the usual method. The error in rate constant was found to be about 3% and estimated error in $\Delta E^{\neq}$ was $\pm$ 0.8 k.cal.mole^{-1}.

Results and Discussion

The rates of reaction were found to be first order in acetophenone, catalyst and zero order in iodine. The pseudo-first order rate constants at different temperatures and the activation parameters are given in Table 1. $\Delta S^{\neq}$ values are all negative and vary in a significant manner. The negative entropy values obtained for the activation process are indicative of a more rigid structure in the transition state than in the reactants.

TABLE 1—RATE CONSTANTS FOR THE IODINATION OF ACETOPHENONES AT DIFFERENT TEMPERATURES CATALYSED BY ACETATE BUFFER AND ACTIVATION PARAMETERS AT 35° IN 50% $MeOH-H_2O$.

Acetophenone = 5×10^{-2} *M*; Iodine = 5×10^{-3} *M* / $\mu = 0.6$ *M* Acetate Buffer = 0.5 *M*; Temperature = 35°

Acetophenone	Rate constant $k \times 10^5$ sec^{-1} 30°	35°	40°	45°	$\Delta H^{\neq}$ k. cal. mole^{-1}	$-\Delta S^{\neq}$ E.u.
H	1.15	1.59	3.22	5.25	18.8	19.4
p-Cl	2.55	4.34	7.39	12.13	19.6	14.9
m-NO_2	14.70	26.86	50.66	82.61	21.1	6.5
p-NO_2	23.96	44.86	77.96	137.40	21.9	1.4

Hammett Relationship: The rate constants for the reactions of each carboxylate anion with different acetophenones were correlated by the 'σ^-' values gave a series of Hammett plots at 35° in 50% $MeOH-H_2O$ as shown in Fig 1. The 'ρ' values and thus the sensitivity of the reaction to the substituents in the aceto-

* Present Address : Department of Chemistry, Arts and Science College, Warangal-506010.

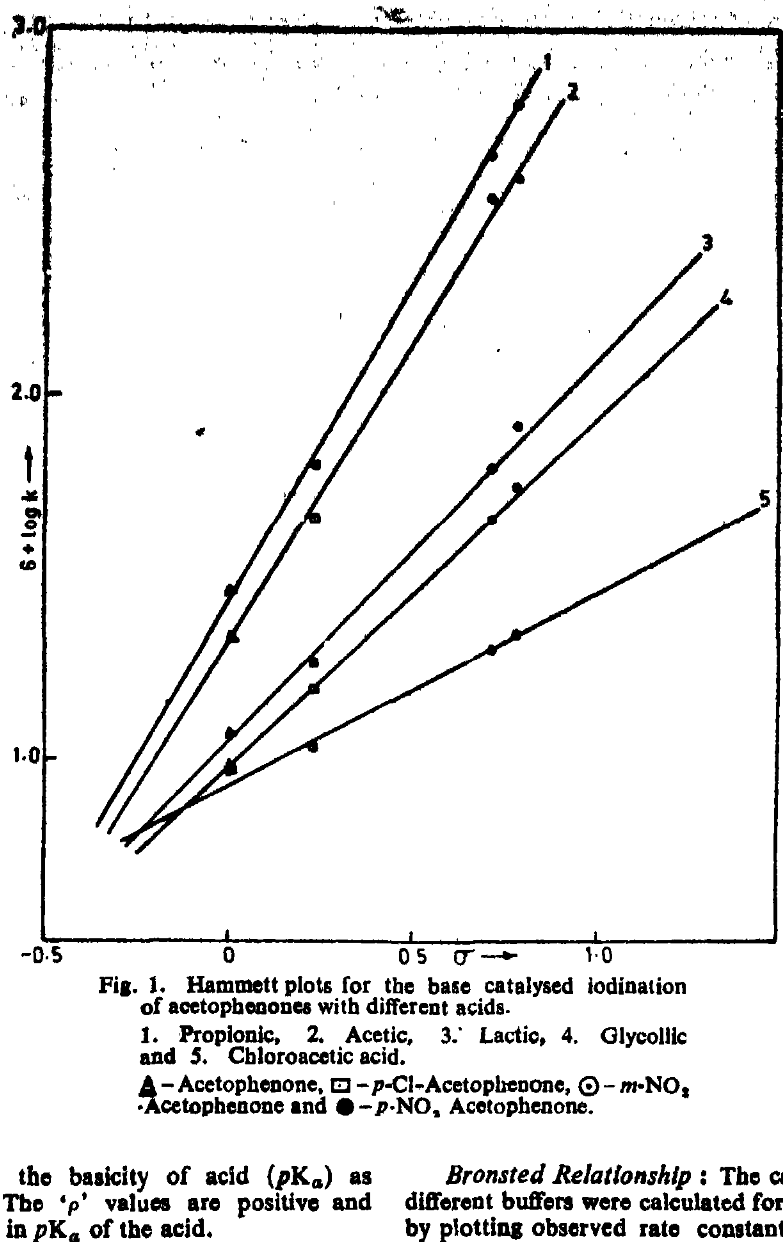


Fig. 1. Hammett plots for the base catalysed iodination of acetophenones with different acids.

1. Propionic, 2. Acetic, 3. Lactic, 4. Glycollic and 5. Chloroacetic acid.

▲ – Acetophenone, ☐ – *p*-Cl-Acetophenone, ⊙ – *m*-NO_2-Acetophenone and ● – *p*-NO_2 Acetophenone.

phenones, depends on the basicity of acid (pK_a) as shown in Table 2. The 'ρ' values are positive and increase with increase in pK_a of the acid.

TABLE 2—THE HAMMETT REACTION CONSTANT (ρ) FOR THE IODINATION OF ACETOPHENONES AND THE OBSERVED IONISATION CONSTANTS (pK_a) OF DIFFERENT ACIDS IN 50% $MeOH-H_2O$ AT 35°

Acid	pK_a	ρ	*r
Propionic acid	5.65	1.77	0.9973
Acetic acid	5.37	1.66	0.9988
Lactic acid	4.57	1.06	0.9982
Glycolic acid	4.50	0.97	0.9996
Chloroacetic acid	3.65	0.57	0.9922

*Regression coefficient.

Bronsted Relationship : The catalytic constants of different buffers were calculated for each acetophenone by plotting observed rate constant against buffer salt concentration at a given *p*H in 50% $MeOH-H_2O$ at 35° (Table 3). The ionisation constants of propionic, acetic, lactic, glycollic and chloroacetic acids were determined in 50% (v/v) $MeOH-H_2O$ at 35° The obtained data obeys the Bronsted equation. The plot of logarithm of catalytic constant versus pK_a of acid gave a series of Bronsted plots and the corresponding Bronsted slopes 'β' are tabulated in Table 3. The Bronsted coefficient 'β' provides a measure of the sensitivity of the reaction to the basicity of the acid and depends on the electron attracting power of the substituents in acetophenone. Table 3 indicates that as 'σ' values increase from - H to *p*-NO_2, 'β' values also increase.

Mechanism : The mechanism of the reaction of iodination of acetophenone with base (carboxylate

TABLE 3—CATALYTIC CONSTANTS OF DIFFERENT CARBOXYLATE BUFFERS AND THE BRONSTED COEFFICIENT 'β' OF EACH ACETOPHENONE IN 50% MeOH–H_2O AT 35°.

Acetophenone $= 5\times10^{-3}$ M; Iodine $= 5\times10^{-4}$ M / $\mu = 0.6$ M

Acetophenone	β	*r	Catalytic constant $k_a \times 10^3 M^{-1}$, Sec^{-1}				
			Propionic	Acetic	Lactic	Glycolic	Chloroacetic
H	0.32	0.9978	6.25	4.90	2.95	2.82	1.41
p-Cl	0.47	0.9962	15.00	12.70	4.68	3.89	1.70
m-NO_2	0.84	0.9856	104.50	67.61	13.40	11.22	2.29
p-NO_2	0.88	0.9993	136.25	81.25	16.52	13.50	2.57

*Regression coefficient.

anion) as a catalyst can reasonably be formulated as a bimolecular nucleophilic attack of B^- (carboxylate anion) on carbonyl carbon. The effect of structural variations in carboxylate anion and in acetophenone is apparent from Hammett and Bronsted plots. The 'ρ' values obtained are positive ranging from 0.57 to 1.77 (Table 2.), indicating that the presence of electron-attracting groups in the ring favours the nucleophilic attack at carbonyl carbon, because of the decrease in electron density at the reaction centre. The Bronsted slopes 'β' obtained are in the range of 0.32 to 0.88. A high β value (near to 1.0) indicates a high degree of proton transfer to the catalysing base in the transition state and a low value indicates a low degree of proton transfer[4]. The order of reactivity of the acetophenones from Bronsted slopes confirmed as p-NO_2 > m-NO_2 > p-Cl > H. The 'β' and 'ρ' values are not equal but show a regular variation. This can be understood in terms of changes in bond formation B. . . . .C at carbonyl carbon and bond breaking C. . . . .H in methyl group adjacent to carboxyl carbon, in the transition state with the changes in electron withdrawing ability of the substituents[6].

Acknowledgement

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Molecular Adsorption and Ion-Exchange of Weak Organic Electrolytes on Ion-Exchange Resin

L. POCHHALI* and S. K. ADHIKARY

Physical Chemistry Laboratory, Chemistry Department, Jadavpur University, Calcutta—700032, India

and

K. C. RAY

Chemistry Department, Visva – Bharati, Santiniketan, West Bengal, India

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The molecular adsorptions of some carboxylic fatty acids, as well as chloro-substituted acetic acids together with hydrochloric acid on the Cation-exchange resin, Amberlite-IR-120 in its hydrogen form have been studied. It has been found that the adsorption increases in the order, hydrochloric < formic < acetic < n-propionic < monochloroacetic < n-butyric < dichloroacetic < trichloacetic. Also with the same ion-exchange resin, the simultaneous ion-exchange as well as molecular adsorptions of liberated acids from solutions of sodium, potassium and magnesium salts of carboxylic acids have been investigated and the results computed.

THE ion-exchange properties of synthetic ion-exchange resins from solutions of electrolytes containing counter-ions different from that in the resins, have been extensively studied[1,2,3,4]. The resins also possess the property of adsorbing non-electrolytes and electrolytes molecularly from their solutions[5,6,7,8]. In cases of weak electrolytes like the aliphatic carboxylic acids, both ion-exchange and molecular adsorption take place simultaneously. Though in these cases, ion-exchange and adsorption have been investigated but rarely differentiation has been made between the two. Starobinets and Gleim[9] studied the ion-exchange and adsorption of aliphatic carboxylic acids on anion-exchange resins in their halide forms and it is they who first differentiated between ion-exchange and molecular adsorption.

When a solution of an aliphatic carboxylic acid is equilibrated with the hydrogen form of a cation exchanger, there will be no ion-exchange but the acid will be molecularly adsorbed on the resin. But when a solution of a salt of an aliphatic carboxylic acid is equilibrated with the hydrogen form of a cation-exchanger, the hydrogen ion in the exchanger will of course, be exchanged with the counter-ion in the salt solution and an equivalent amount of a free acid will, be formed in the solution but a part of the free acid will be molecularly adsorbed on the resin.

This paper presents the results of investigation of pure molecular adsorption of hydrochloric acid, straight chain aliphatic acids ranging from formic to n-butyric acids as well as three chlorosubstituted acetic acids on the hydrogen form of a cation-exchanger. An attempt has also been made in this paper to differentiate between molecular adsorption and ion-exchange by using solutions of sodium, potassium and magnesium salts of formic to n-butyric acids with the same cation exchanger. In all these cases Amberlite-IR-120 (PSSA with 8% DVB) in the hydrogen form was used.

Experimental

The strongly acidic cation-exchanger, Amberlite-IR-120 with a nominal content of 8% divinyl benzene was conditioned first by converting the commercial resin into sodium form with about 1*N* sodium hydroxide and then reconverting the resin into its hydrogen form by treatment with about 2*N* HCl. In between these processes the material was washed thoroughly with water. The resin in its hydrogen form was finally washed by passing double distilled water through the column containing resin until the resin was free from any foreign ion. This was checked by *p*H measurement of the washed water. The resin was then dried in air and kept in a closed container. The exchange capacity, and the moisture content of the moist resin were then determined. The exchange capacity in the H-form resin was (4.91 ± 0.04) meq/gm, dry resin for the different lots.

The aliphatic carboxylic acids ranging from formic to n-butyric as well as the three chloro-substituted acetic acids and the hydrochloric acid, were all "analar grades" and used without any purification. About 2 gms. of the air-dried resin (of known moisture contents) were taken in bottles with ground glass stoppers into which 50 ml of acid solutions of known concentrations were added. The mixtures were shaken for 4 hours and then kept for 48 hours to ensure attainment of equilibrium. The final concentrations of the equilibrated acid solutions were determined and from the difference between the initial and final concentrations, the adsorptions of acids per gm of dry resin

* Senior Author

were calculated. The concentrations of the acids were found out by alkalimetric titration using phenolphthalein as indicator.

Sodium formate, acetate and n-propionate of "analar grade" were used without purification. But sodium salt of n-butyric acid was prepared by adding analar sodium carbonate into the corresponding "analar" acid. The acid was taken in slight excess. The solution containing the sodium salt was then evaporated to dryness, washed carefully with double distilled water and finally recrystallised from water. The potassium salt solutions of the aliphatic carboxylic acids were prepared by adding equal volumes of equinormal solutions of potassium hydroxide to the corresponding acids. The concentrations of sodium and potassium salt solutions were determined by conductometric titrations with standard hydrochloric acid.

The magnesium salt solutions were prepared by adding "analar" magnesium oxide in slight excess to the corresponding acids and then filtering out the solutions. The concentrations of the magnesium salt solutions were determined by titrating with standard EDTA solutions using Eriochrome Black-T indicator.

As in the determination of adsorption, 50 ml of salt solutions of different concentrations were added to about 2 gms. of air-dried resin (of known moisture content) and allowed to attain equilibrium as before. The final concentrations of salt solutions were determined in aliquots by conductometric titrations in the cases of sodium and potassium salts and EDTA titration in the case of magnesium salts. From the difference between initial and final concentrations of salt solutions, the ion-exchanges per gm of dry resin were calculated by the formula,

$$\text{Exchange} = \frac{(C_i - C_e) \times 100}{(100 - W) \times W_R} \times V \text{ meq/g dry resin} \quad (1)$$

Where, C_i = initial conc. of salt solution in eqv. per litre.

W_R = weight of resin in gms.

W = water content in weight per cent.

V = solution volume in ml.

C_e = equilibrium conc. of salt solution in eqv. per litre

The concentrations of the liberated acids were determined in the separate aliquots by alkalimetric titration. These acid concentrations were subtracted from the differences between initial and final concentrations of the salt solutions. From the subtracted values the adsorptions of liberated carboxylic acids per gm of dry resin were calculated as,

$$\text{Adsorption of liberated acid} = \frac{[(C_i - C_e) - C_A] \times 100 \times V}{(100 - W) \times W_R} \text{ meq/g. dry resin} \quad (2)$$

where, C_A = Conc. of liberated acid in eqv./litre.

Before doing these experiments the analytical methods employed were tested with salt solutions of known concentrations as well as mixtures of salt solutions and carboxylic acids of known concentrations. The results were found to be satisfactory within experimental error.

To see whether a salt of a carboxylic acid is adsorbed by the same salt form of the resin, experiments were performed with sodium form of the resin and sodium acetate solutions of different concentrations. It was found, within experimental error, that no adsorption takes place in these cases.

All these experiments were performed in room temperatures (30 ± 2°).

Results and Discussion

The experimental adsorption isotherms of carboxylic acids (formic to n-butyric), as well as, those of mono-, di- and trichloroacetic acids on the cation-exchange resin, Amberlite-IR-120, in its hydrogen form are presented in fig 1. For comparison, the isotherm for hydrochloric acid have also been included in this figure.

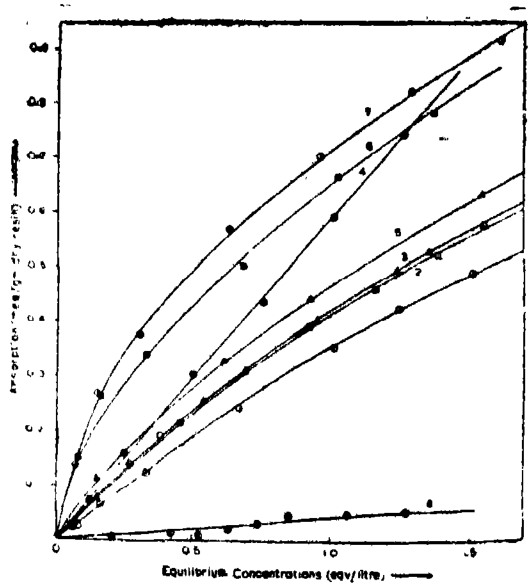


Fig. 1. Adsorption Isotherms of Carboxylic Acids on the hydrogen form of Amberlite-IR-120.
1. Formic, 2. Acetic, 3. Propionic, 4. n-butyric, 5. monochloro-acetic, 6. dichloro-acetic, 7. trichloro-acetic, 8. Hydrochloric.

The adsorption results for formic, acetic, propionic and n-butyric acids are in agreement with those found by Bhatnagar et al[5], Reichenberg & Wall[7], and Starobinets & Kharevich[11]. The adsorption increases with the chainlength of the carboxylic acids, i.e ; formic<acetic<propionic<n-butyric. Reichenberg and Wall[7] explained their results from the standpoint of London dispersion interactions between the hydrocarbon part of the adsorbate molecules and benzene nuclei of the resin. The interaction and hence the adsorption increase with increasing chainlength of the carboxylic acids. Schneider, Kresheck and Scheraga[10] from their studies on the thermodynamic parameters, e.g ; standard free energy, enthalpy and entropy of the interactions between the carboxylic acids and a hydrocarbon network of polystyrene, concluded that the molecular adsorption should increase with the chainlengths of the carboxylic acids, by a mechanism involving hydrophobic effect and consequent decrease in the structure of water. Starobinets and Kharevich[11] measured the adsorption of aliphatic monocarboxylic acids on a cation-exchange resin in the absence of ion-exchange process. Their results also indicate an increase in adsorption with the number of $-CH_2$ groups in the acids. They also invoked the hydrophobic bond formation to explain their results.

The adsorption of the strong acid, HCl, is very small as shown in figure 1. From the results of the experiments with the sodium form of the resin with sodium acetate solutions with concentrations from $1.5M$ to $0.3M$, it has been seen that the amount of acetate ion adsorbed is zero within experimental error. This shows that the undissociated form of the carboxylic acids is only adsorbed. The same conclusion was reached by Schneider *et al*[10] who used sodium butyrate solution. The adsorption of carboxylic fatty acids is, therefore, expected to be a function of both the chainlength and dissociation constant. Carboxylic acids having higher dissociation constants should be less adsorbed by the resin. The dissociation constants[12] of the carboxylic acids used, decreases in the order, formic $(1.77\times10^{-4})>$ acetic $(1.77\times10^{-5})>$n-butyric $(1.54\times10^{-5})>$propionic (1.34×10^{-5}). Although the dissociation constant of n-butyric acid is slightly greater than that of propionic acid, it is more strongly adsorbed than the latter. Of the two opposing effects, the chainlength and dissociation constant, the effect of the dissociation constant is possibly more than compensated by the effect of chainlength in the case of n-butyric acid.

To examine the effect of dissociation constants on the adsorption, the adsorption of chloro-substituted acetic acids on the same cation-exchange resin has been studied. In these acids, the chain-length may be assumed to remain same as in acetic acid whereas the dissociation constant[12] increases considerably with the number of chlorine atoms in the acids. So it is to be expected that the order of adsorption would be, acetic>monochloroacetic>dichloroacetic>trichloroacetic. But actually just the opposite order has been found : acetic<monochloroacetic<dichloroacetic<trichloroacetic. It is quite unlikely that the chloro-substituted acetic acids have higher hydrophobicity than that of acetic acid. So it seems that the mechanism of adsorption in these cases is somewhat complicated. There may be some kind of interaction between the chlorosubstituted group with the hydrocarbon matrix of the resin.

The results of the experiments on ion-exchange and simultaneous adsorptions of liberated free acids by the hydrogen form of the resin with the sodium, potassium and magnesium salts of carboxylic acids are shown in figures 2, 3 and 4 respectively. From the consideration of the dissociation constants[12] of the carboxylic acids,

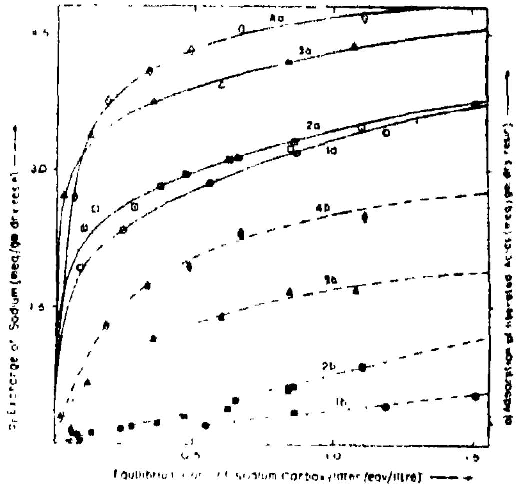


Fig. 2. a) Ion-Exchanges of Sodium Carboxylates and b) Adsorptions of corresponding liberated acids on the hydrogen form of Amberlite-IR-120.

1. Sodium formate, 2. Sodium acetate, 3. Sodium propionate, 4. Sodium n-butyrate.

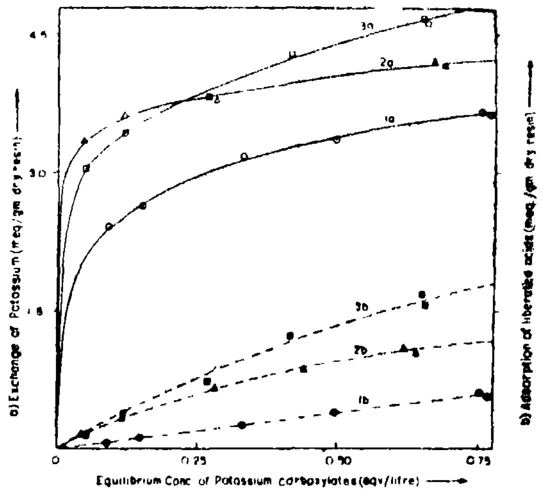


Fig. 3. a) Ion-Exchanges of Potassium carboxylates and b) Adsorptions of corresponding liberated acids on the hydrogen form of Amberlite-IR-120.

1. Potassium acetate. 2. Potassium Propionate, 3. Potassium n-butyrate.

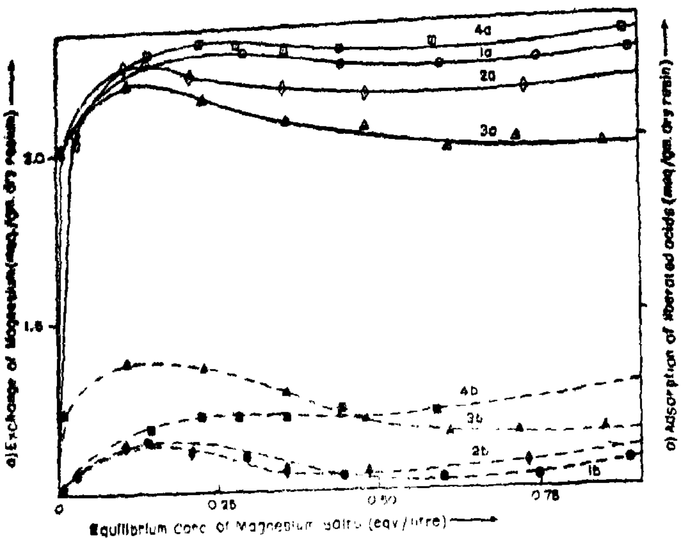


Fig. 4. a) Ion Exchanges of Magnesium Carboxylates and b) Adsorptions of corresponding liberated acids on the hydrogen form of Amberlite-IR-120

1. Magnesium formate, 2. Acetate, 3. Propionate, 4 n-butyrate.

It is expected that lower the dissociation constant, higher will be the exchange of the cation from the salt solutions. This is borne out in the cases of sodium and potassium salts in dilute solutions, e.g ; formate< acetate<n-butyrate<propionate. But at higher concentrations, the position of propionate and n-butyrate is reversed, e.g ; propionate<n-butyrate. Here also the effect of dissociation constant is overcome by the effect of chainlength of the butyrate ion in concentrated solution. The adsorption of the liberated acids runs parallel to the ion-exchange from the corresponding salt solutions : higher the ion-exchange, higher the adsorption ; the adsorption increases with increase in the chainlength of the carboxylic acid, as is found in the case of pure molecular adsorption of the carboxylic acids on the hydrogen form of the same cation-exchange resin.

The magnesium salt solutions of the carboxylic acids present a different picture. With increasing concentration of the salt solutions both the ion-exchange and adsorption of the liberated acids at first increase, then decrease and afterwards tend to increase very slowly showing a maxima in the curve (fig. 4). There is no regularity of ion-exchange or adsorption with the chainlength or dissociation constant of the carboxylic acids. This is possibly due to formation of complex between magnesium and carboxylate ions.

The behaviour of three different salts of the n-butyric acid are compared in fig. 5 ; with the salts of other acids same type of figures may be drawn. The results obtained from these figures are summarised in the table I.

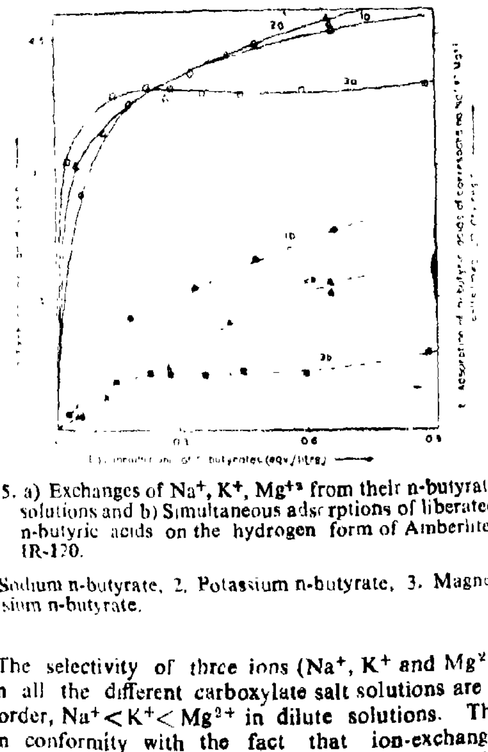


Fig 5. a) Exchanges of Na^{+}, K^{+}, Mg^{+2} from their n-butyrate solutions and b) Simultaneous adsorptions of liberated n-butyric acids on the hydrogen form of Amberlite-IR-120.

1 Sodium n-butyrate, 2. Potassium n-butyrate, 3. Magnesium n-butyrate.

The selectivity of three ions (Na^{+}, K^{+} and Mg^{2+}) from all the different carboxylate salt solutions are in the order, $Na^{+} < K^{+} < Mg^{2+}$ in dilute solutions. This is in conformity with the fact that ion-exchanger prefers the counter-ion of higher valence and larger size and the preference increases with dilution of the solution[18]. The same order of selectivity of these cations over hydrogen from cation-exchange resins has been found by many earlier workers. In concentrated solutions, the position of the Mg^{2+} ion comes down

TABLE-1

Salt Solutions	Concentration		Selectivity of Ions	Adsorption of liberated acid from the salts
Acetate :	Dilute range	:	$Na^+ < K^+ < Mg^{2+}$	Na ≈ K < Mg
	Conc. range	:	$Na^+ < Mg^{2+} < K^+$	Mg < Na < K
Propionate :	Dilute range	:	$Na^+ < K^+ < Mg^{2+}$	K < Na < Mg
	Conc. range	:	$Mg^{2+} < Na^+ < K^+$	Mg < K < Na
n-butyrate :	Dilute range	:	$Na^+ < K^+ < Mg^{2+}$	K < Mg < Na
	Conc. range	:	$Mg^{2+} < Na^+ < K^+$	Mg < K < Na

due to the formation of complex, as mentioned earlier. As regards the adsorption of liberated acids in the case of acetate solutions, more acid is adsorbed from potassium salt than from sodium one. But from propionate and n-butyrate salt solutions, their position is reversed, adsorption of acid is greater from sodium salts than from potassium salts. The behaviour of magnesium salts again is different in dilute and in concentrated solutions due to the same reason as mentioned already.

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Studies on the Dissociation Constants of Benzoic Acids in Methanol and Water Mixtures by Conductometric Methods

A. K. MANDAL and S. C. LAHIRI

Department of Chemistry, Kalyani University, West Bengal, India.

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The pKa values of benzoic acid and substituted benzoic acids in metanol + water mixtures (8-75.9 wt. % of methanol) were determined using modified conductometric method suggested by Gelb with slight change. The results have been further verified by Fuoss-Kraus method. The limitations of the present state of knowledge of solution chemistry in accounting the variations of the dissociation constants with solvent composition have been stressed.

THE determination of ionization equilibria in mixed solvents has received considerable attention. The potentiometric method utilizing the hydrogen electrode as reference electrode is difficult and can be applied only in absence of complicating reduction reactions The method also suffers from the inherent limitation that the e.m.f. of standard hydrogen electrode is taken to be zero in all the solvent systems and at all temperatures. This, however, as rightly pointed out by Popovych[1], generates quite a large number of thermodynamically unrelated pH or e.m.f. scales as there are solvents making the correlation of pK values in different solvents difficult.

Recently, Panichajakul and Woolley[2] suggested a rapid and convenient method for determination of weak acids in aquo-organic mixed solvents using glass-electrodes assuming that the glass electrode junction potentials, asymmetry potentials and responses do not change with solvent composition and the electrolytes are completely dissociated in the mixed solvents.

In search of a suitable method which could give ionization constants avoiding difficulty and assumptions, we found that the conductometric method as suggested by Gelb[3] can be utilized with success in mixed solvents with little modification. In this paper, we report the dissociation constants of benzoic, *m*-fluoro, *m*-chloro and *p*-bromo benzoic acids in methanol water mixtures. The results have been further verified by Fuoss-Kraus method[4,5].

Experimental

Methanol (E. Merck) was purified and the weight percentages of methanol in alcohol-water mixtures and their relative permitivities were determined in the same way as described before[6,7]. Benzoic acid (G. R., E. Merck), *m*-chloro-benzoic acid (Puriss, Fluka), *m*-fluoro-benzoic acid (Purum, Fluka) and *p*-bromo benzoic acid (Purum, Fluka) were all crystallised from alcohol. The purity of the samples was tested by melting-point determination. The organic acids and perchloric acid (G. R., E. Merck) were estimated volumetrically in the usual way. Caustic soda, succinic acid and potassium hydrogen phthalate were of E. Merck's G. R. grade. Conductivity water was obtained by redistilling the distilled water with alkaline permanganate from all glass distilling set. Care has been taken to avoid contamination of water and solvents with CO_2.

The conductometric 'titration' of benzoic acid with $HClO_4$ and the blank 'titration' were performed in the same way as described before[8]. The ionic strengths of the solutions were kept as low as practicable ($\approx 10^{-4} M$ to $10^{-3} M$). The experiment was repeated several times with different concentrations of benzoic acid (ranging from 1×10^{-4} to $1 \times 10^{-3} M$). Similar measurements were made in different percentages of methanol-water mixtures (0 to 75.9% by wt. of methanol) and with *m*-chloro-, *m*-fluoro- and *p*-bromo-benzoic acids.

For the determination of dissociation constants by Fuoss-Kraus method, the conductances of the different concentrations of these acids (Concentration range $10^{-4} M$ to $10^{-2} M$) were measured several times making appropriate corrections for the conductances of the solvents.

Conductance measurements were made with the aid of a Leeds and Northrup Model 4959 conductance bridge with a sensitivity of 0.1%. A 50-60 cycle signal was employed. A dip-type conductance cell (cell constant $= 0.85$ cm^{-1}) was used. The measurements were performed at $25° \pm 0.02°$.

Results

For a mixture of completely dissociated $HClO_4$ and partly dissociated HA, the dissociation constant for the reaction

$$HA \rightleftharpoons H^+ + A^- \quad (1)$$

can be written as

$$K = \frac{\alpha(\alpha C_{HA} + C_{HClO_4}) \times f^2_\pm}{(1-\alpha)}$$

the terms have their usual significance. However, when the conductances of the mixture (1/R) (containing HA and $HClO_4$) and blank solutions ($1/R^*$) (containing $HClO_4$ only) are equal, we have (following Gelb[8])

$$C_{HClO_4} \cdot \Lambda'_{HClO_4} + \alpha C_{HA} \cdot \Lambda'_{HA} = C^*_{HClO_4} \cdot \Lambda'^*_{HClO_4}$$

and $\quad C_{HClO_4} + \alpha C_{HA} = C^*_{HClO_4}$

assuming $\Lambda'_{HClO_4} = \Lambda'_{HA}$ and $\Lambda'_{HClO_4} = \Lambda'^*_{HClO_4}$

in aqueous and mixed solvents from which α can be calculated. Λ' = Equivalent conductance of the completely dissociated electrolyte at any ionic strength and Λ = The equivalent conductance of the electrolyte at that ionic strength i.e. $\Lambda = \alpha \Lambda'$

($\alpha = 1$, in case of $HClO_4$ and * indicates the quantities in blank solutions).

We have kept ionic strength sufficiently low and the variations of ionic strengths are too small to vitiate the Λ values appreciably. However, refinements of K values are possible taking

$$\alpha = (C^*_{HClO_4} - C_{HClO_4})/\beta C_{HA}$$

$$\text{where } \beta = \frac{\Lambda'_{HA}}{\Lambda'_{HClO_4}}$$

The procedure as suggested by Gelb to calculate β is rather cumbrous. We, therefore, adopted an alternative procedure to calculate β values. The $\Lambda°$ values of HA and $HClO_4$ in mixed solvents were determined as given below. The ratio $\Lambda°_{HA}/\Lambda°_{HClO_4}$ gives β directly since the ionic strength and the concentrations of HA and $HClO_4$ are low. β-values are likely to be of the same order of magnitude in water as well as in different mixed solvents, as the variations of mobility of anions in different solvents are likely to follow the similar pattern. The results are given in table 1.

The dissociation constant values have also been checked in the following way.

$\Lambda°$ values of perchloric acids in different mixed-solvents have been determined in the same way as described before[8]. The initial values of $\Lambda°_{HA}$ and K of weak acids in mixed solvents were determined from the plot of ΛC against $1/\Lambda$ of a number of dilute solutions of HA utilizing the equation

$$\Lambda C = -K\Lambda° + K\Lambda°^2/\Lambda$$

($\Lambda°$ = Equivalent conductance at infinite dilution). The improvement in the values of $\Lambda°_{HA}$ and K were made using the method of Fuoss and Kraus[4,5]. The plots of $F(Z)/\Lambda$ against $\Lambda C f^2_\pm F(Z)$ showed good straight lines wherefrom K and $\Lambda°$ values were calculated utilizing the equation

$$F(Z)/\Lambda = \frac{1}{K\Lambda°^2} \cdot \frac{\Lambda C f^2_\pm}{F(Z)} + \frac{1}{\Lambda°}$$

The values of the constants in the Onsager equation were calculated from the interpolated values of viscosities and dielectric constants of methanol-water mixtures from the data given by Bates and Robinson[9] and F(Z) values were calculated from the computed values of F(Z) using $\Lambda°$ values previously determined.

The log $f_\pm$ values were calculated from the equation

$$-\log f_\pm = A\sqrt{\alpha C}$$

using the appropriate values of A.

Discussions

The average values of $\Lambda°$ and pK of different organic acids in aquo-organic mixtures are given in the table 1. Considering the limitations, the results obtained from titration method and Fuoss-Kraus method agree fairly well. The accuracy of the extrapolated $\Lambda°$ values is known to be rather low. Inspite of the limitations, the $\Lambda°$ values as given in table 1 seem to be quite in order. $\Lambda°$ values decrease as the percentage of organic solvent increases as noted by Shedlovsky[10] et al. It is also observed that $\Lambda°$ values are higer in methanol-water mixtures compared to those in ethanol-water mixtures as expected. The pK values of benzoic acid in methanol-water mixtures have been reported by Bacarella et al[11]. Our results show that the agreement is excellent upto 54.20% or even upto 75.94% by wt. of methanol considering the limits of accuracy (± 0.04 in water to ± 0.10 in higher percentages of mixed solvent). However, the values determined by pH-titration or potentiometric method seem to be a bit high compared to conductometric method in aquo-organic mixtures as evinced from the pK_a values of acetic acid in methanol-water mixtures determined potentiometrically and conductometrically[10].

The results show a good linearity when pK is plotted against mole-fractions of organic solvent or $1/\epsilon$ upto about 65 wt % of organic solvents. Deviations are apparent at high percentages. Marginal improvement occurs when the activities of water are taken into consideration as suggested by Yasuda[12].

TABLE 1

Wt.% of MeOH	Mole fraction of MeOH	(1/ε) ×100	Λ° mhos Cm^2/eqv					pKa of benzoic			pKa of *m*-F.B.A.			pKa of *m*-C.B.A.			pKa of *p*-B.B.A.		
			$HClO_4$	B. A.	F.B.A.	C.B.A.	B.B.A.	(a)	(a*)	(b)	(a)	(a*)	(b)	(a)	(a*)	(b)	(a)	(a*)	(b)
8.0	0.0000	1.27	415.0	392.5	390.6	391.8	386.0	4.17	4.20	4.21	3.84	3.87	8.86	3.81	3.84	3.85	3.94	3.94	3.98
8.0	0.0470	1.33	381.0	360.0	365.0	358.0	355.7	4.30	4.32	4.31	3.94	3.98	3.98	3.92	3.95	3.98	4.12	4.15	4.16
16.0	0.0968	1.40	331.3	308.0	312.0	307.0	302.9	4.45	4.50	4.51	4.10	4.18	4.22	4.12	4.20	4.23	4.25	4.30	4.34
25.2	0.1593	1.48	280.5	263.1	263.0	259.0	260.0	4.66	4.75	4.75	4.32	4.42	4.45	4.25	4.34	4.38	4.40	4.49	4.53
34.4	0.2279	1.57	228.0	218.0	214.0	216.0	212.7	4.88	4.98	5.01	4.56	4.66	4.64	4.54	4.59	4.62	4.68	4.75	4.77
44.7	0.3126	1.69	195.1	182.0	180.0	185.0	178.0	5.14	5.21	5.25	4.73	4.80	4.83	4.70	4.80	4.82	4.85	4.96	4.95
54.2	0.3997	1.84	171.7	157.0	148.0	152.0	155.0	5.39	5.50	5.53	5.00	5.10	5.12	5.00	5.05	5.09	5.11	5.21	5.24
64.1	0.5000	2.01	151.5	137.5	139.0	135.7	140.0	5.64	5.76	5.76	5.25	5.36	5.35	5.20	5.30	5.35	5.40	8.52	5.54
75.9	0.6392	2.25	131.0	118.0	115.0	119.5	121.0	5.92	6.02	6.07	5.56	5.68	5.71	5.	5.60	5.62	5.57	5.72	5.75

B.A.=Benzoic acid, F.B.A.=*m*-fluoro benzoic acid, C.B.A.=*m*-chloro benzoic acid, B.B.A.=*p*-bromo benzoic acid.

a) average pKa values from plotting of ΛC vs. (1/Λ ; a*) average pKa values from Fuoss-Kraus method.

b) average pKa values from 'titration' method.

The approximate difference of pk-values in mixed solvents can be had from Born[13] equation

$$\Delta pK = pK(s) - pK(w) = 121.6\ (1/\epsilon - 0.0128)(1/r_A + 1r_H)$$

(r_A and r_H represent the radii of the acid anion and proton respectively). However. $\Delta\ pK$ values calculated with $r_H = 0.86$ Å[14] and $r_A = 0.55$ Å[9] do not agree with the experimental values. This may be due to (i) uncertain values of radii, (ii) approximate nature of the equation. Furthermore, (iii) solute-solvent interactions and solvent-basicity have not been taken into consideration. Modifieations of the Born equation which take into account of the local variations in dielectric constant within the solvation shells make some improvement[15-17]. The theory of Hiromi[18] which takes into account the particular geometry and charge distribution within organic ion is also inadequate as it predicts the variation of pK against $1/\epsilon$.

The difference between $[pK(s) - pK(w)]_R$ and $[pK(s) - pK(w)]_0$ [where R=substituted acid and O= unsubstituted acid] should be linearly related to $1/\epsilon$ as expected from the equation but actually not observed in practice

$$[pK(s) - pK(w)]_R - [pK(s) - pK(w)]_0$$

$$= 121.6\ (1/\epsilon - 0.0128)\ (1/r_{AR} - 1/r_{A0})$$

The equation cancels the term due to free-energy of transfer of H^+ ions and therefore, is likely to be obeyed as the observed deviations have generally been assumed to be due to the free-energy of transfer of proton from water to different alcohol mixtures which is not a linear function of $1/\epsilon$[19].

It is imperative that the proper knowledge of the "non-electrostatic" contributions resulting from the interactions between the solute species with solvent molecules is necessary to understand the behaviour of solvents. It is natural that structural modifications and ionic solvation and complications arising from the equilibria of the type

$$H_3O^+ + MeOH \rightleftharpoons H_2O + MeOH_2^+$$

has pronounced effect. Furthermore, the free-energy of transfer of proton from water to methanol + water mixtures upto 50% w/w methanol has been regarded to be due to the transfer of a tetrahedral-aquo proton from water into the mixture and subsequent replacement of an H_2O molecule by CH_3OH molecule[20].

$$H^+(H_2O)_4\ _{solv} + CH_3OH\ _{solv} \rightleftharpoons H^+(H_2O)_3 \cdot CH_3OH_{solv} + \text{Water}$$

Further replacement of water molecule by CH_3OH molecule is possible but we have no definite knowledge of the various interactions and displacement process. The question of anion solvation is intriguing and evading.

The $\Delta\ pK_a$ values of all thesea acids are the same within limits of experimental yccuracy. Since the acids are of the samo charge tpes with the same ionizing group having almost the same size, an approximate equality of "medium effect" is expected. A little variation, however, may be explained as due to the preferential solvation of uncharged acids by methanol molecules and ions by water molecules. It is expected that the ratios of water molecules in the solvation shells of uncharged acids and particularly of anions are changed considerably by the presence of the strongly polar substituent in the benzene ring. Polar substituents will have a natural tendency to increase the water molecules in the solvation shells of anions compared to uncharged acids leading to a favourable free-energy change. The structural modifications and ionic solutions will also have profound effect.

In fine, we stress the need of determining the dissociation constants of weak acids in mixed solvent by conductometric methods with bettter bridges and find out the reliabilities of different methods. These may prove useful to find out unambiguous method of determining the dissociation constants in mixed solvents free from assumptions.

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Conductometric Studies on the Dissociation Constants of Salicylic and Substituted Salicylic Acids in Methanol-Water Mixtures

A. K MANDAL and S. C. LAHIRI

Department of Chemistry, University of Kalyani, Nadia, West Bengal, India.

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The pKa values of salicylic acid and 5-chloro- and 5-Bromo-salicylic acids in methanol+water mixtures (8 - 87.9 wt % of methanol) were determined using conductometric method suggested by Gelb with slight modification. The results have been further verified by Fuoss-Kraus method. The limitations of the present state of knowledge of solution chemistry in accounting the variations of the dissociation constants with solvent composition have been stressed.

THE role of solvents on the ionization constants of weak acids is not well understood. The changes in pK-values with solvent composition cannot be explained in terms of Born equation[1] or modified equations[2-5]. It has been well emphasized that the changes in $\triangle$pK values can only be accounted for in terms of 'electrostatic' and 'non-electrostatic' parts[6,7]. But in view of the limited accuracy of the equations and in absence of accurate values of radii of ions particularly for the unsymmetrical ones, it is very difficult to realize the full significance of 'non-electrostatic' parts or medium effects of the solvents.

These imply the usefulness of determining the dissociation constants of more acids and bases in mixed solvents for a proper knowledge of 'electrostatic' and 'non-electrostatic' parts and to have a proper correlation of the results.

We have emphasized previously[8,9] the limitations of determining the dissociation constants in mixed solvent using H electrode or glass electrodes. These are :

a) The e.m.f. of hydrogen electrode is taken to be zero in all the solvent systems. This generates quite a large number of unrelated *p*H or e.m.f. scales[10]. The values of dissociation constants are obviously difficult to correlate.

b) Liquid junction potentials, asymmetry potentials and responses of the glass electrodes do not change with solvent composition.

Furthermore, the reliability of the results should be checked by different methods. The search for a suitable alternative showed that the method suggested by Gelb[11] could be utilised with success in mixed solvents with slight modification.

We report in this communication, the dissociation constants of salicylic acid, 5-chloro- and 5-bromo-salicylic acids in methanol + water mixtures (0-87°/$_o$ by wt of methanol) by Gelb's method. The results have been further verified by Fuoss and Kraus[12,13] method involving no assumptions.

Experimental

Methanol (G.R., E. Merck) was purified and the weight percentages of methanol in the solvent mixtures were determined in the same way described before. Conductivity water was prepared in the way given before[14,15]. Precautions were taken to prevent the solvents from contamination with CO_2. Salicylic acid (G.R , E. Merck), 5-chlorosalicylic acid (BDH) and 5-bromo salicylic acid (BDH) were purified from alcohol. The purity of the acids was tested by melting point determination. The acids and $HClO_4$ (G.R., E. Merck) were estimated volumetrically using NaOH (G R., E. Merck) standardized with succinic acid (G.R., E. Merck) and Potassium hydrogen phthalate in the usual way.

The experimental details are the same as described before[8,9].

Conductance measurements were made with the aid of a Leeds-Northrup model 4959 conductance bridge with a sensitivity of $\pm$ 0.1°/$_o$. A 50-60 cycle signal was employed. A dip-type Philips conductance cell with cell constant (θ=0.85 cm^{-1}) was utilized. The measurements were done at 25 $\pm$ 0 02°.

Results

The dissociation constant of a weak acid HA

$$HA \rightleftharpoons H^+ + A^- \quad (1)$$

in presence of completely dissociated $HClO_4$ can be written as

$$H = \frac{\alpha(\alpha C_{HA} + C_{HClO_4}) \times f_{\pm}^2}{(1-\alpha)} \quad (2)$$

The terms have their usual significance. However, when the conductances 1/R (of the mixture containing $HClO_4$ and HA) and $1/R^*$ (blank solutions containing $HClO_4$ only) are equal, we have,

$$C_{HClO_4} \cdot \Lambda'_{HClO_4} + \alpha C_{HA}\, \Lambda'_{HA} = C^*_{HClO_4} \cdot \Lambda'^*_{HClO_4} \quad (3)$$

$$\text{and} \quad C_{HClO_4} + \alpha C_{HA} = C^*_{HClO_4} \quad (4)$$

assuming

$$\Lambda'_{HClO_4} = \Lambda'^*_{HClO_4} \text{ and } \Lambda'_{HClO_4} = \Lambda'_{HA}$$

in aqueous and mixed solvents from which α can be calculated.

Λ' = Equivalent conductance of the completely dissociated electrolyte at any ionic strength.

Λ = equivalent conductance of the electrolyte at that ionic strength i.e., $\Lambda = \alpha \Lambda'$

($\alpha = 1$, in case of $HClO_4$ and * indicates the quantities in blank solutions).

Further improvement of K values is possible taking

$$\alpha = (C^*_{HClO_4} - C_{HClO_4})/\beta C_{HA} \quad (5)$$

Where $\beta = \Lambda'_{HA}/\Lambda'_{HClO_4}$

β can be approximated to $\Lambda^\circ_{HA}/\Lambda^\circ_{HClO_4}$

at low concentrations of the acid and at low ionic strengths.

$\Lambda^\circ_{HClO_4}$ values have been taken from our previous experiment.

The initial values of Λ°_{HA} and K of weak acids in mixed solvents were determined from the plot of ΛC against $1/\Lambda$ in the usual way. The improvement of Λ°_{HA} and K values were made using the method of Fuoss and Kraus[12,13] utilizing the relationship

$$F(Z)/\Lambda = \frac{1}{K\Lambda^{\circ 2}} \cdot \frac{\Lambda c f_{\pm}^2}{F(Z)} + \frac{1}{\Lambda^\circ} \quad (6)$$

as described before[8,9,16].

The log $f_\pm$ values were calculated from the equation

$$-\log f_{\pm} = A\sqrt{\alpha C} \quad (7)$$

using the appropriate values of A.

Discussions

The average values of Λ° and pK of salicylic acids in methanol + water mixtures are given in table 1. Considering the limitations, the results obtained from titration method and Fuoss-Kraus[12,13] method agree fairly well. Inspite of the limited accuracy of extrapolated Λ° values, the results seem to be quite in order. Λ° values decrease as the percentage of organic solvent increases as noted by Shedlovsky et al[17]. Λ° values have been found to be higher in methanol + water compared to those in ethanol + water mixtures as expected.

The pK-values of salicylic acid and substituted salicylic acids have been found to be higher in methanol + water mixtures than in the corresponding ethanol + water mixtures[16] at low percentages (upto about 60 wt %). This is anomalous in view of lower dielectric constants of ethanol + water mixtures compared to methanol + water mixtures and generally the pK-values increase with decrease in dielectric constant. However, the reverse trend is observed at higher percentages as expected. The expected trend is also observed in case of benzoic acids.

Though most of the results (the pK-values in ethanol + water mixtures and the corresponding pK-values in methanol + water mixtures) are within the limits of our experimental accuracy, but the anomalous results may be due to the change in the nature of hydrogen-bonding.

It is well-known that the dielectric constant alone is incapable of accounting for the change in pK-values and the main factor being solute-solvent interactions of which the hydrogen-bonding will be of special importance in the present case. It may be that the internal hydrogen-bond formation in stabilizing the anion is more pronounced in ethanol + water mixtures than in methanol + water mixtures.

A linear relationship is observed when pKs are plotted against mole-fraction of organic solvent or $1/\epsilon$ upto about 65 wt % of organic solvents. Deviations are observed at high percentages. Slight improvement occurs when the activities of water are taken into consideration as suggested by Yasuda[18].

The approximate difference of pK values in mixed solvents can be had from Born[1] equation

$$\Delta pK = pK(S) - pK(W) = 121.6\,(1/\epsilon - 0.0128)\,(1/r_A + 1/r_H) \quad (8)$$

TABLE 1

Wt. % of MeOH	Mole fraction of MeOH	$1/\epsilon \times 100$	Temp. 25°C Λ° in mhos cm^2/eqv. HClO$_4$	Salicylic	C.S.A.	B.S.A.	Av. pKa of Salicylic (a)	(a*)	(b)	Av. pKa of C.S.A. (a)	(a*)	(b)	Av. pKa of B.S.A. (a)	(a*)	(b)
0.0	0.0000	1.27	415.0	400.0	395.0	394.1	3.04	3.05	3.04	2.65	2.66	2.66	2.61	2.62	2.66
8.0	0.0466	1.33	381.0	362.4	361.0	364.0	3.12	3.16	3.16	2.76	2.78	2.77	2.75	2.78	2.79
16.0	0.0968	1.40	331.3	309.0	305.2	209.0	3.24	3.37	3.37	2.80	2.87	2.90	2.86	2.92	2.95
25.2	0.1593	1.48	280.5	269.0	26.82	264.0	3.45	3.56	3.58	3.04	3.10	3.12	3.06	3.13	3.16
34.4	0.2279	1.57	228.0	219.0	220.0	219.5	3.54	3.64	3.69	3.17	3.27	3.28	3.19	3.28	3.32
44.7	0.3126	1.69	195.1	186.0	184.6	184.0	3.74	3.85	3.87	3.43	3.42	3.44	3.32	3.45	3.48
54.2	0.3997	1.84	171.7	155.8	156.0	158.0	3.92	4.00	4.05	3.53	3.59	3.60	3.52	3.59	3.62
64.1	0.5000	2.01	151.5	137.0	134.0	135.2	4.18	4.30	4.30	3.70	3.75	3.78	3.63	3.73	3.74
75.9	0.6392	2.25	131.0	114.4	113.5	116.0	4.48	4.50	4.56	3.92	3.95	4.02	3.95	4.00	4.03
87.9	0.8034	2.57	117.5	96.2	93.5	93.0	4.73	4.79	4.82	4.15	4.20	4.23	4.17	4.22	4.28

C.S.A.=5-chlorosalicylic acid, B.S.A.=5-bromosalicylic acid.
a) pKa from the plot of ΛC vs $1/\Lambda$, a*) pKa from Fouss-Kraus method.
b) pKa from titration method.

where r_A & r_H represent the radii of acid anion & proton respectively. However, pK values calculated with r_H= 0.86A°[2] and r_A=2.0 A°[19] do not agree with the experimental values. The reasons are—(i) uncertain values of radii of ions, (ii) approximate nature of the Born equation, (iii) solute-solvent interactions and solvent basicity of uncertain magnitude affecting the results. The improvement is only marginal even if the local variations in dielectric constant within the solvation shells have been taken into consideration[2-5]. Even the theory of Hiromi[20] which takes into account the particular geometry and charge distribution within organic ion is inadequate as it predicts the variation of pK against $1/\epsilon$.

The difference between $[pK(S)-pK(W)]_R$ and $[pK(S)-pK(W)]_O$ [Where R=Substituted acid and O=unsubstituted acid] should be linearly related to $1/\epsilon$ as expected from the equation but actually not observed in practice.

$$[pK(S)-pK(W)]_R-[pK(S)-pK(W)]_O=121.6\ (1/\epsilon-0.0128)\ (1/r_{AR}-1/r_{AO}) \qquad (9)$$

The equation cancels the term due to free-energy of transfer of H^+ ions and therefore, is likely to be obeyed as the observed deviations have generally been assumed to be due to the free-energy of transfer of proton from water to different alcohol mixtures which is not a linear function of $1/\epsilon$[21].

Ohtaki[22] has shown that a good account of the variation of pK for charged acids in alcohol-water mixtures can be obtained by combining the Born equation with terms which depend upon a knowledge of hydronium-alkoxonium ion equilibria in the solvent mixtures. The treatment reduces to equation (9) for the comparison of medium effects for two charged acids. However, the relationship fails and the treatment does not help much for the comparison of the relative behaviour of pair of acids as observed by Rochester[21].

The failure of the equation is also apparent as the value of the dielectric constant is known to be a function of radii of ions[3-5,23].

The results indicate that the proper knowledge of the 'non-electrostatic' contributions resulting from ion-solvent interactions, solvent-basicity, hydrogen-bonding etc. are necessary to explain the variations of pK with solvents.

The $\triangle$pKa (=pKs − pKa) values or "medium effects of all these acids are the same within the limits of experimental accuracy as expected in the ionizing group, charge and sizes are almost the same in all the cases. A slight variation in $\triangle$pK values may result from the change in the ratios of water in the solvation shells of anions having polar substituents compared to uncharged acids leading to a favourable free energy change. The structural modification of solvation shells due to ionic solvation will have profound effect.

But from the results we are yet unable to throw more light on the role of solvents on the dissociation constants of acids and bases. We also emphasize the need of determining dissociation constants of weak acids by conductometric methods with more accurate bridges and better facilities. These possibly may evolve a suitable and unambiguous method of determining the dissociation constants in aquous and mixed solvents free from assumptions.

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Synthesis of 3,4-Dihydro-5,6-Dimethoxyisocoumarin

JAGDISH N. SRIVASTAVA

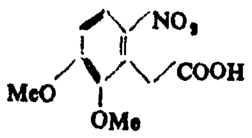
Post Graduate Department of Chemistry, Bhagalpur University, Bhagalpur-812007.

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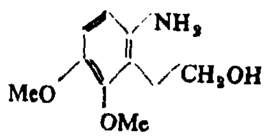
2-Nitro-*o*-homoveratric acid has been prepared by direct nitration of *o*-homoveratric acid. The nitro acid was successively reduced with lithium aluminium hydride and sodium dithionite to 2-amino-*o*-homoveratryl alcohol. On diazotisation, Sandmeyer reaction and hydrolysis it gave 3,4-dihydro-5,6-dimethoxyisocoumarin.

3,4-DIHYDRO-5, 6-dimethoxyisocoumarin has earlier been synthesised by the oxidation of 5,6-dimethoxyisochroman[1]. The same compound has now been prepared by the procedure adopted in the synthesis of mellein methylether[2]. For this purpose 2-nitro-*o*-homoveratric acid[8] was obtained by direct nitration of *o*-homoveratric acid in 24% yield. The identity of nitro acid was established by comparsion with an authentic sample prepared by the earlier route[8].

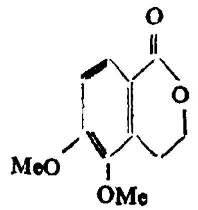
In the synthesis of 3,4-dihydro-7,8-dimethosyisocoumarin[4], it has been shown that lithium aluminium hydride reduction of methyl 2-homoveratrate afforded a mixture of 2,3,2′3′-tetramethoxy-6,6′-dihydroxyethylazobenzene and 2-nitrohomoveratryl alcohol, which as such or separately when reduced with sodium dithionite, gave 5,6-dimethoxy-2-aminophenethyl alcohol.



I



II



III

Accordingly, adopting the same procedure the nitro acid (I) was reduced successively with lithium aluminium hydride and sodium dithionite to yield 5,6-dimethoxy-2-aminophenethyl alcohol (II), isolated as its hydrochloride. Finally, diazotisation of (II), its conversion into nitrile which was not purified and subsequent hydrolysis, followed by acidification, gave 3,4-dihydro-5,6-dimethoxyisocoumarin(III).

Experimental

M. Ps. are uncorrected

2-Nitro-o-homoveratic acid (I) :-*o*-Homoveratric acid (5g) was added portion wise to nitric acid (25 ml., d 1.42) with constant stirring, the temperature during addition was not allowed to rise above 0°. After addition was complete, the reaction mixture was left at 10° for 1 hr. and then poured into a large volume of ice water. The precipitate was filtered, washed free of acid. Crystallisation from methanol afforded a yellow solid which melted between 108-16°. Repeated fractional crystallisation from methanol gave yellow needles of (I) (1.5g), m.p. 179-80°, undepressed on admixture with an authentic sample prepared by a different route[3]. The mother liquor furnished a yellow crystalline solid (2g), mp. 158-60°.

2-Amino-o-homoveratryl alcohol (II) : A solution of 2-nitro-*o*-homoveratric acid (1.5g) in dry tetrahydrofuran (25 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (0.8g) in dry tetrahydrofuran (25 ml) cooled to 10° and left for 2 hr. at room temperature. Excess of lithium aluminium hydride and complex were decomposed by careful portionwise addition of ice-water followed by 2 N-H_2SO_4 (?0 ml). It was extracted with ether (3x50 ml). The combined extract was dried over potassium carbonate and evaporated to a dark red gum which was dissolved in methanol (25 ml) and water (20 ml). Sodium dithionite (2g) was added in two lots, when the dark red colour discharged to straw yellow colour. The solution was refluxed on water bath for a few minutes. After distilling most of methanol, the solution was extracted with chloroform (3x25 ml), the chloroform solution was extracted with 50% hydrochloric acid (2x25 ml). The acid solution was chilled mixed with chloroform (25 ml), basified carefully with ammonia, chloroform layer was separated and the aqueous layer was further extracted with chloroform (2x25 ml). The combined extract was dried over sodium sulphate and the solvent distilled to give a red oil which turned dark due to rapid oxidation in air. It was taken up in dry ether (25 ml), chilled and dry hydrogen chloride bubbled through when the amine hydrochloride (0.28g) separated as dark green needles.

It was sublimed (bath temp. 150°/1 mm) as white needles, m.p. 188-90°, decomposes with previous darkening. (Found : C, 51.0 ; H, 6.2% : $C_{10}H_{16}O_3NCl$ Requires C, 51.3 ; H, 6.4%).

3,4-Dihydro-5,6-dimethoxyisocoumarin (*III*) : The hydrochloride of 2-amino-*o*-homoveratryl alcohol (0.2g) in hydrochloric acid (0.2 ml ; d 1.16) and water (5 ml) was diazotised with sodium nitrite (0.08g) in water (0.6 ml) at 0°. After neutralisation with sodium carbonate, the diazonium solution was added to a solution of potassium cyanide (0 2g), nickel chloride (0.18g) and sodium carbonate (0.1g) in water (6 ml) at 18° with stirring. The mixture was allowed to stand for 1 hr. and then heated to 80° for half an hour. The solution was cooled extracted with ether (3x20 ml), the combined extract was dried over sodium sulphate and ether distilled to give a red gum. The gummy material was refluxed with aqueous potassium hydroxide (10 ml ; 10%) for 2 hr., cooled and acidified with hydrochloric acid. The solution was filtered and extracted with chloroform (2x25 ml), the extract dried over sodium sulphate and the solvent evaporated to give a gum which solidified after a few hours. It was sublimed in vacuo (bath temp. 100-5°/1 mm) to yield a white residue. Recrystallisation from ethyl acetate-petroleum ether afforded colourless needles (0.10g), m.p. 72-73°, undepressed on admixture with an authentic sample prepared by a different route[1]. IR in $CHCl_3$: 5.88μ (conjugated 8 lactone).

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Synthesis of New Mero- and Asymmetrical Pyrazolo-Monomethine Cyanine Dyes.

ZARIF H. KHALIL and ABDU E. ABDEL-RAHMAN

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt, A.R.E.

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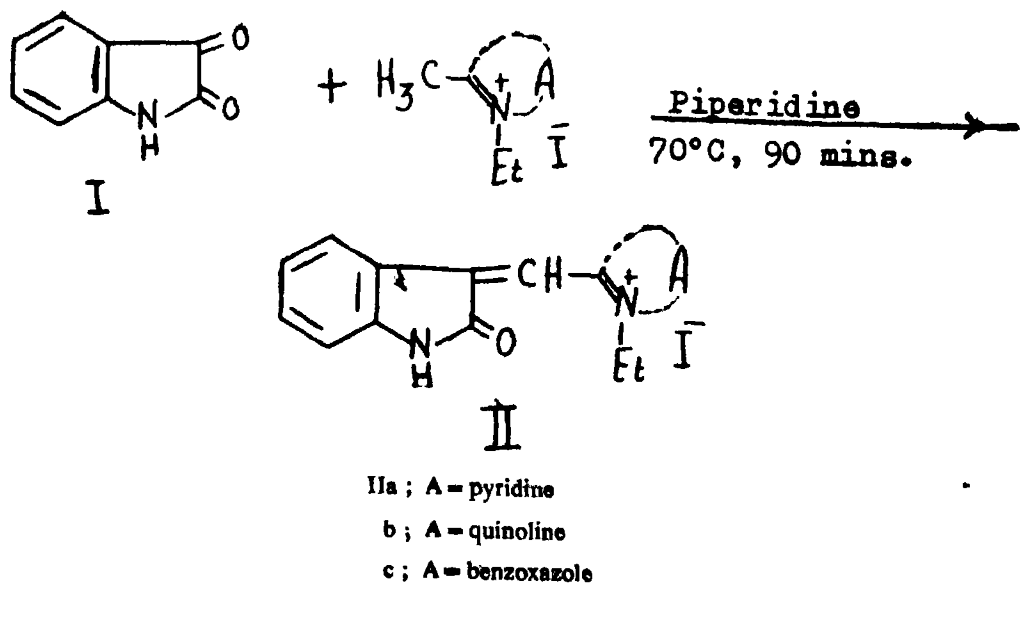
New isatylidine mero cyanine dyes (II) were prepared through the reaction of isatin (I) with 2-methyl quaternary salts in presence of a basic catalyst. Interaction of 3-methyl-1-phenyl-5-pyrazolone derivatives (III) with α-picoline- and quinaldine-ethiodides in presence of triethylamine afforded the asymmetrical pyrazolo-2′-monomethine cyanines (V). Meanwhile, the use of piperidine gave the aldol intermediate (IV), which dehydrated to the corresponding cyanine dye (V). Structural configurations were identified by i.r. and v.s. spectral determination.

MERO cyanine dyes containing cyclic keto group which are listed in the literature are beyond estimation, and they are used as photosensitisers[1-6], electron acceptors[4], electrophotography[7] and filter dyes[4,8]; but, those containing isatylidine residue was not mentioned before. Recently, it was stated by B. Lal, *et al*[9]. that the condensation reaction of pyridine-2,3- and 4-carboxaldehyde with substituted 2-oxindole gave the corresponding 3-isatylidine derivatives, and the 2-pyridyl isomer possesses high diuretic activity. Within these respects, 3-isatylidine-2-(pyridino-, quinolino- and benzoxazolo-ethiodides)-mero cyanine dyes(II) were prepared.

Also, asymmetrical pyrazolo-2′-monomethine cyanine dyes(V) were obtained through the reaction of 5-pyrazolone derivatives with 2-methyl quaternary salts in presence of triethylamine. On the other hand, the use of piperidine, gave the aldol intermediate (IV), which dehydrated to the corresponding cyanine dye (V)[10]. It is of interest to mention that, the asymmetrical-2′-monomethine cyanine dyes are widely used as photosensitisers in the blue-green light[11-14].

Results and Discussion

The condensation reaction between 2-methyl quaternary salts and isatin (I) takes place at the more active 3-carbonyl group (within isatin nucleus) in presence of a basic catalyst, giving 3-isatylidine-2′-(pyridino-, quinolino-, and benzoxazolo-ethiodides) mero cyanine dyes(II). The reaction is represented as follows :



IIa ; A = pyridine

b ; A = quinoline

c ; A = benzoxazole

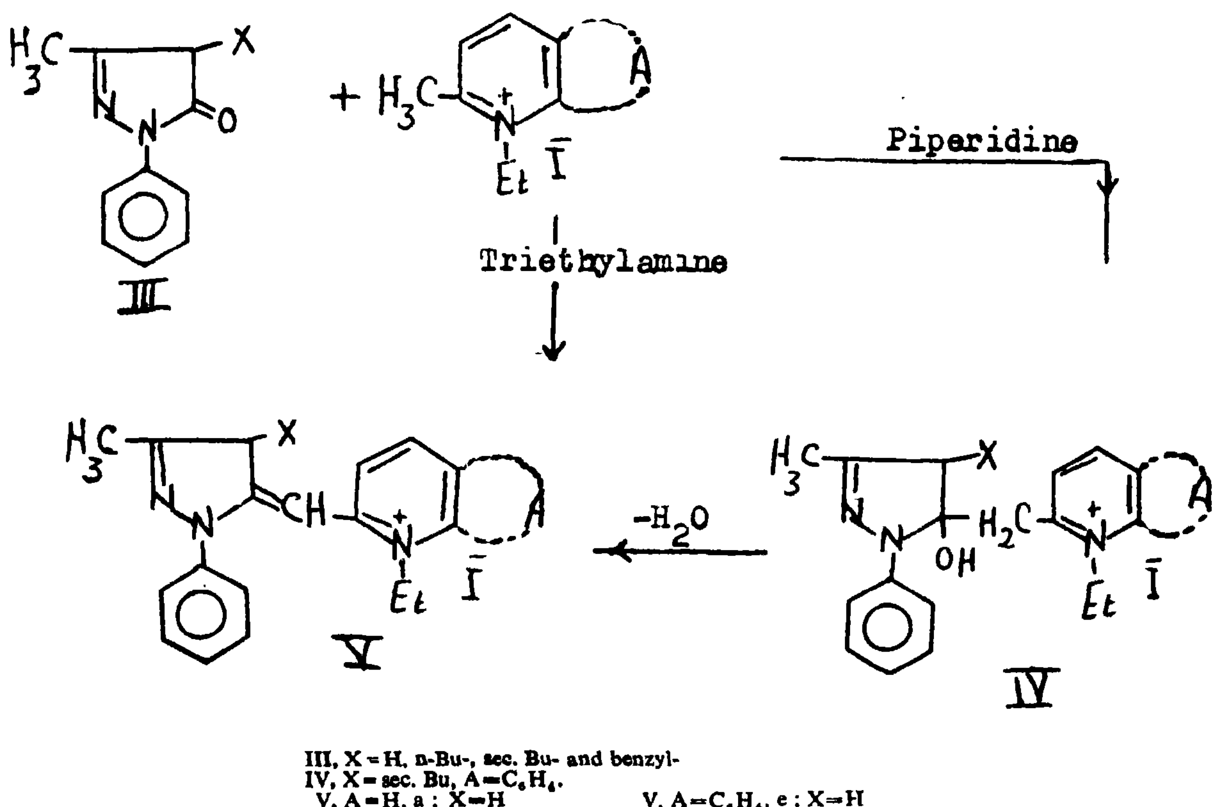
The mero cyanine dyes (IIa-c) are readily soluble in polar organic solvents with an orange to violet colour and their ethanolic solutions gave a yellow colour in acidic medium turned violet on basification with alkali hydroxide. The reversible change in colour gives an indication to their use as acid-base indicator in protometric titrations. IR spectra of (IIa-c) showed a well defined absorption band at ~1725 – 1703 cm^{-1} attributed to α-β unsaturated ketone in a 5-membered ring.

The v.s. absorption spectra of (IIa, A=pyridine) in ethanol showed a strong absorption band located at λ_{max} 405 nm, ϵ_{max} 14,000 with a shoulder at λ_{max} 385 nm, ϵ_{max} 13,690 and another band at a longer wavelength attributed to intramolecular charge transfer (C.T.) located at λ_{max} 550 nm, ϵ_{max} 4,950. Substituting of the quaternary heterocyclic moiety, pyridyl-by quinolyl- (IIb, A=quinoline) causes a strong red shift in the longer wave length (C.T.) by 120 nm, with the

TABLE 1—3-ISATYLIDINE-2′-[PYRIDINO-, QUINOLINO-BENZOXAZOLO-ETHIODIDES]-MEROCYANINE DYES (IIA-C)

Compound No.	m. p. °C.	Solvent of crystallisation	Yield % theory	Formula	Analysis % Calcd N	Analysis % Found N	Absorption spectra λ_{max}	Absorption spectra ϵ_{max}
IIa	300	Ethanol	45	$C_{16}H_{15}N_2OI$	7.40	7.28	385 (sh), 405, 550	13,690 ; 14,000 4,950
IIb	247	Methanol	58	$C_{20}H_{17}N_2OI$	6.54	6.48	430, 525 (sh), 565, 610 (sh), 670	600, 630, 770, 420, 118
IIc	300	n-Butanol	37	$C_{18}H_{15}N_2O_2I$	6.69	6.73	256, 374, 412 (sh), 546	20,400 ; 23,000, 20,150 ; 16,600

The analysis for carbon and hydrogen are satisfactory, (sh)=shoulder.



III, X = H, n-Bu-, sec. Bu- and benzyl-
IV, X = sec. Bu, A = C_6H_4.
V, A = H, a ; X = H; b ; X = n-Bu-; c ; X = sec.Bu; d ; X = benzyl-
V, A = C_6H_4, e ; X = H; f ; X = n-Bu; g ; X = sec.Bu; h ; X = benzyl

decrease in its molar extension coefficient, λ_{max} 670 nm, ϵ_{max} 118. While, substituting by benzoxyazolyl-, causes a slight blue shift by 4 nm with strong intensification of the absorption band, (IIc, A=benzoxazole) λ_{max} 546 nm, ϵ_{max} 16,600 (c.f Table 1).

The reaction of 5-pyrazolone and its 4-alkyl derivatives (III) with α -picoline- and quinaldine-ethiodides was found to be greatly affected by the reaction conditions and the type of basic catalyst used. Thus, the use of triethylamine, the condensation reaction proceeded to give directly the expected asymmetrical 5-[3-methyl-1-phenyl-(4-alkyl substituted) pyrazolo]-2'-[pyridinium (quinolinium) 1-ethiodide] monomethine cyanines (V) ; while, using piperidine, the aldol intermediate (IV) was isolated here thermally dehydrated to the corresponding cyanine dye (V). The reaction is shown :

The aldol intermediate is colourless needles, readily soluble in alcohols and its i.r. spectra showed a well defined absorption band at ~3520 cm^{-1} attributed to OH group.

The asymmetrical pyrazolo-2'-monomethine cyanines (V) possess different colours ranged from orange to deep violet, easily soluble in concentrated sulphuric acid from which iodine was liberated on heating. Cyanine dyes containing quaternary quinoline residue (Ve-h ; A=C_6H_4) exhibit a strong green flourescence in solutions, which was not observed in those containing quaternary pyridine residue (Va-d, A = H).

The v.s. absorption spectra of (V, A = C_6H_4) in ethanol consist of different bands, their position and molar extinction coefficient are influenced by the type of 4-substituent (X) in the pyrazolo nucleus. The absorption spectra of (Ve, X=H) shows an absorption band at λ_{max} 375 nm, ϵ_{max} 1,100 and another band at a longer wave-length attributed to intramolecular charge transfer (C.T.) located at λ_{max}. 478 nm, ϵ_{max} 1,800. Substituting 4-hydrogen by n-butyl (Vf, X=n-Bu) causes a strong red shift in C.T. band by 90 nm ; λ_{max} 568, ϵ_{max} 5,500. This red shift is attributed to the increase in both mass molecule and its coplanarity. On the other hand, substituting by sec-butyl (Vg, X= sec. Bu) having the same mass molecule, causes a slight blue shift relative to (Ve, X = H) by 3 nm; λ_{max} 475 nm, ϵ_{max} 17,490. This blue shift may be due to the bulky effect of the branched alkyl side chain (i.e. due to the α-substituted methyl group) which affect the coplanarity of the molecule leading to the increase in the excitation energy, absorbing at a shorter wave-length (cf. Table 3).

Experimental

The i.r. spectra were determined with a Perkin-Elmer Infrared 137 B. Spectrophotometer, v.s. spectra were recorded on a Unicam SP 8000' ultraviolet recording spectrophotometer using 1 cm matched silica cells. Melting points are not corrected.

Synthesis of 3-isatylidine-2'-[pyridino-, quinolino- and benzoxazolo-ethiodides]-mero cyanines (II) : A mixture of 2-methyl quaternary salt (α-picoline-, quinaldine-and 2-methyl benzoxazole-ethiodides) (0.006 mol), isatin (I) (0.005 mol), ethanol (50 ml) and piperidine (~one ml) was heated for 90 minutes at 70°. The reaction mixture was concentrated to ~30 ml at reduced pressure where the mero cyanine dyes (II) were separated, they were collected, washed with few ml. methanol, then with ether and crystallised from the proper solvent. The results are given in Table 1.

Synthesis of asymmetrical 5-[3-methyl-1-phenyl-(4-alkyl substituted) pyrazolo]-2'-[pyridinium) (quinolinium)-1-ethiodide]-monomethine cyanine dyes (V) : A mixture of α-picoline-(quinaldine) ethiodides (0.006 mol), 3-methyl-1-phenyl-(4-substituted alkyl)-5-pyrazolone (0.005 mol), triethylamine (1.5 ml) and ethanol (50 ml) was refluxed for 3 hours on a water bath. The reaction mixture was concentrated to ~20 ml. and poured onto a stirred ice-cold dilute sulphuric acid. The separated cyanine dyes (V) were collected, washed with water, then with ether and crystallised from the proper solvents. The results are given in Tables 2 and 3.

TABLE 2—ASYMMETRICAL 5-[3-METHYL-1-PHENYL-(4-ALKYL)-PYRAZOLO]-2'-[PYRIDINIUM-1-ETHIODIDE]-MONOMETHINE CYANINE DYES (Va–d) (A = H).

Compound No.	m. p. °C	Solvent of crystal	Yield % theory	Formula	Analysis % Calcd.	Found	Absorption spectra	
					N	N	λ_{max}.	ϵ_{max}.
Va	156	Methanol	42	$C_{18}H_{20}N_3I$	10.87	10.18	394	4,500
Vb	159	Ethanol	51	$C_{22}H_{28}N_3I$	9.11	8.97	345, 500 (sh)	5,400 ; 4,400
Vc	130	Ethanol/water	38	$C_{22}H_{28}N_3I$	9.11	9.23	390	5,100
Vd	90	,, ,,	40	$C_{25}H_{24}N_3I$	9.48	9.35	496 (sh)	11,700

The analyses for carbon and hydrogen are satisfactory.

TABLE 3—ASYMMETRICAL 5-[3-METHYL-1-PHENYL-(4-ALKYL)-PYRAZOLO]-2'-QUINOLINIUM-1-ETHIODIDE] (Ve–h, A = C_6H_4).

Compound No.	m.p. °C	Solvent of crystallisation	Yield % Theory	Formula	Analysis % Calcd N	Analysis % Found N	Colour of ethanolic solution H_2SO_4 (0.1 N)	Colour of ethanolic solution NaOH (0.1 N)	Absorption spectra λ_{max}	Absorption spectra ϵ_{max}
Ve	199	Ethanol	67	$C_{22}H_{22}N_3I$	9.23	9.32	Yellow	Orange red	375, 478	1,100 ; 1,800
Vf	108	Methanol	72	$C_{26}H_{20}N_3I$	8.22	8.14	Yellow	Violet	428 (sh), 506 568	3,225 ; 4,540 5,500
Vg	140	Ethanol/ether	55	$C_{26}H_{20}N_3I$	8.22	8.00	Yellow	Orange	378, 475	9,900 ; 17,490
Vh	110	Ethanol/ether	65	$C_{29}H_{28}N_3I$	7.70	7.64	Yellow	Violet	325, 480 (sh), 518, 560	4,175 ; 2,630 4,300 ; 5,980

The analyses for carbon and hydrogen are satisfactory.

Synthesis of the aldol intermediate (IV) : A mixture of quinaldine ethiodide (0.006 mol), 3 methyl-1-phenyl-4-sec. butyl-5-pyrazolone (III), ethanol (50 ml) and piperidine (1·5 ml) was refluxed for 3 hours on a water-bath. The reaction mixture was concentrated and cooled, where colourless needles were separated after 3 days at room temperature. The product was collected, washed with alcohol, then with ether and crystallised from ethanol-water mixture (1 : 1) into colourless needles, m.p. 108°, yield 42%. Analysis calculated for $C_{26}H_{32}N_3OI$: N,7.93. Found : 7.87%.

Dehydration of (IV) was carried out by heating the solid material at 123–5° for 15 minutes. The cyanine dyes (V) has a m.p. and mixed m.p. 140°.

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Chemistry of Isodithiobiurets, Part II. Oxidative De-*p*-Chlorobenzylation as an Alternative Route to the Synthesis of 3,5-Diaryl/Arylalkylimino-1,2,4-Dithiazolidines.

RAJENDRA SINGH and V. K. VERMA

Applied Chemistry Section, Institute of Technology, Banaras Hindu University, Varanasi-5.

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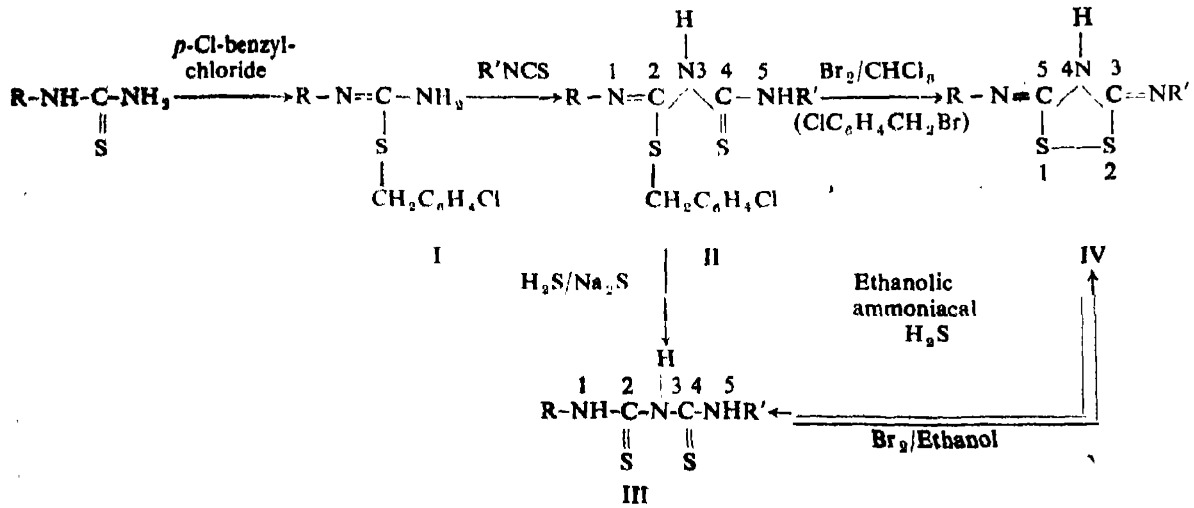
5-Phenylimino-3-*p*-tolylimino-, 5-phenylimino-3-*m*-tolylimino-, 5-phenylimino-3-*p*-ethoxyphenylimino-, 5-phenylimino-3-*p*-Cl-phenylimino- and 5-phenylimino-3-ethylimino-1,2,4-dithiazolidines have been synthesised by the oxidative de-*p*-chlorobenzylation and simultaneous ring closure of the corresponding 1,5-diaryl/arylalkyl-2-S-*p*-Cl-benzyliso-4-thiobiurets.

THE facile oxidative deallylation and cyclisation in various S-allylisodithiobiuret systems leading to the formation of the related 1, 2, 4-dithiazolidines/dithiazolines[1-3] has led us to search for some new alkyl groups which could easily be knocked off from the sulphur of the isodithiobiuret system under oxidizing conditions. In this connection, it was thought of considerable interest to study the behaviour of the *p*-Cl-benzyl group in 1,5-disubstituted isodithiobiuret system.

In the present communication, we report the preparation of certain 1, 5-diaryl/arylalkyl-2-S-*p*-Cl-benzyliso-4-thiobiurets (II) and their successful oxidative de-*p*-chlorobenzylation and simultaneous ring closure to the corresponding 3, 5-diaryl/arylalkylimino-1, 2, 4-dithiazolidine (IV).

The compounds (II) were prepared by the condensation of appropriate 1-Aryl-2-S-*p*-Cl-benzylisothiocarbamide (I) with aryl or alkyl isothiocyanate. On reaction with molecular bromine in concentrated chloroform solution, the *p*-chlorobenzyl group of these (II) was eliminated as *p*-chlorobenzylbromide followed by cyclisation to the related 3,5-diaryl/arylalkylimino-1,2,4-dithiazolidine (IV). These (IV) have also been obtained by the oxidation of 1,5-diaryl/arylalkyl-2,4-dithiobiurets (III) which were prepared by reductive de-*p*-chlorobenzylation of the related 2-S-*p*-Cl-benzyliso-4-thiobiurets (II) and also by the reduction of IV with ethanolic ammoniacal hydrogen sulphide. In all the cases, the structures of the compounds III and IV were confirmed by their unequivocal synthesis through alternative routes and were further characterised by mixture melting point technique and by identical I.R. spectra.

The scheme of the reactions is as follows :



where R=phenyl group and R′=*p*-tolyl-, *m*-tolyl-, *p*-ethoxyphenyl-, *p*-Cl-phenyl-and ethyl groups.

Experimental

Preparation of 1,5-diaryl/arylalkyl-2-S-p-Cl-benzyliso-4-thiobiurets (II) : 1-Substituted thiocarbamides were alkylated with *p*-Cl-benzyl chloride. Benzene solution of the 1-substituted-2-S-*p*-Cl-benzylisothiocarbamide free bases were condensed with the appropriate aryl or alkylisothiocyanates resulting in the formation of the corresponding 1,5-diaryl/arylalkyl-2-S-*p*-Cl-benzyliso-4-thiobiurets.

The details of a representative experiment are as follows : 1-Phenylthiocarbamide (5g) was alkylated with *p*-Cl-benzylchloride following Werner's procedure[4]. 1-Phenyl-2-S-*p*-Cl-benzylisothiocarbamide hydrochloride thus obtained was cooled and basified with ammonium hydroxide solution when the free base separated as a solid compound. The product was filtered and dried (yield 9g, 76.5%). Benzene solution of 1-phenyl-2-S-*p*-Cl-benzylisothiocarbamide was mixed with *p*-tolylisothiocyanate (4.7g) in 1:1 mole and refluxed for 1 hr on a water-bath. The semisolid mass so obtained on evaporation of the solvent, was washed with petroleum ether and on addition of a little ethanol, afforded a crystalline mass (yield 8.2g, 63%). It was recrystallised from ethanol m.p. 95°. These compounds are listed in Table-1.

3,5-Diaryl/arylalkyl-imino-1,2,4-dithiazolidines(IV) Oxidative de-*p*-chlorobenzylation of 1,5-diary/larylalkyl-2-S-*p*-Cl-benzyliso-4-thiobiurets with bromine in chloroform: molecular bromine readily effected de *p*-chlorobenzylation of 1,5-diaryl/arylalkyl-2-S-*p*-Cl-benzyliso 4-thiobiurets in a little chloroform solution followed by ring closure to the related 3,5-diaryl/arylalkylimino-1,2'4-dithiazolidine hydrobromides. For example : 1-phenyl-5-*m*-tolyl-2-S-*p*-Cl-benzyliso-4-thiobiuret (3g) was moistened with chloroform (1 ml) and was treated with bromine (1.5g) until colour of bromine persisted. The reaction mixture warmed up considerably evolving fumes of *p*-chlorobenzylbromide. After standing the mixture for 30 minutes, the semi solid product was washed first with ether, then with ether containing a little ethanol, when the hydrobromide of the oxidation product separated as a crystalline mass. On treatment with ammonia, the free base was obtained, which was filtered, dried and thoroughly washed with ether (yield 2.3g, 75%). It was recrystallised from ethanol m.p. 185°. The melting point, yield and elemental analysis of these compounds are given in Table-2.

TABLE 1—PREPARATION OF 1,5-DIARYL/ARYLALKYL-2-S-*p*-Cl-BENZYLISO-4-THIOBIURETS (II)

1-Substituted-2-S-*p*-Cl-benzyl-isothiocarbamide	Isothio-cyanate	1,5-diaryl/aryl-alkyl-2-S-*p*-Cl-benzyliso-4-thiobiuret formed	M. P.	Yield %	Molecular formula	Analysis Found	Reqd.
1-phenyl-2-S-T	*p*-tolyl-isothio-cyanate	1-phenyl-5-*p*-tolyl-B	95	63	$C_{22}H_{20}N_3S_2Cl$	C : 61.91 H : 4.74 N : 9.71	62.04 4.70 9.87
1-phenyl-2-S-T	*m*-tolyl-isothio-cyanate	1-phenyl-5-*m*-tolyl-B	116	61	$C_{22}H_{20}N_3S_2Cl$	C : 62.36 H : 4.42 N : 9.65	62.04 4.70 9.87
1-phenyl-2-S-T	*p*-ethoxy-phenyliso-thiocyanate	1-phenyl-5-*p*-ethoxyphenyl-B	103	60	$C_{23}H_{22}N_3S_2Cl$	N : 8.74 S : 13.39	8.90 13.57
1-phenyl-2-S-T	*p*-Cl-phenyl-isothio-cyanate	1-phenyl-5-*p*-Cl-phenyl-B	120	65	$C_{21}H_{17}N_3S_2Cl_2$	N : 9.27 S : 14.03	9.41 14.35
1-phenyl-2-S-T	Ethyliso-thio-cyanate	1-phenyl-5-ethyl-B	—	50	$C_{17}H_{18}N_3S_2Cl$	—	—

Where T—represents—*p*-Cl-benzylisothiocarbamides and
B—represents—2-S-*p*-Cl-benzyliso-4-thiobiurets.

Typical ir frequencies (cm^{-1}) of 1-phenyl-5-*m*-tolyl-2-S-*p*-Cl-benzyliso-4-thiobiuret :

3166 m, NH stretching (Lit.[6] 3400-3100), 1105 m, 1175 w, N-C(=S)-N grouping (Lit.[5a] 1200-1100) ; 1595 m, N-C=N grouping (Lit.[5b] 1685-1582) ; 1375 vs, C=S grouping (Lit.[6] 1400-1100) ; 700s shows "iso" form in isodithiobiuret chain, 1425 w, CH_2-S deformation (Lit., 1435-1410)[5a,7].

TABLE 2—3,5-DIARYL/ARYLALKYLIMINO-1,2,4-DITHIAZOLIDINES (IV) : OXIDATION OF 1,5-DIARYL/ARYLALKYL-2-S-*p*-Cl-BENZYL-ISO-4-THIOBIURETS WITH BROMINE IN CHLOROFORM.

1,5-diaryl/aryl-alkyl-2-S-*p*-Cl-benzyliso-4-thiobiurets	5-Arylimino-3-aryl/alkylimino-1,2,4-dithiazolidines formed	M. P.	Yield %	Molecular formulae	Analysis Found	Reqd.
1-phenyl-5-*p*-tolyl-B	5-phenylimino-3-*p*-tolylimino-D	175	75	$C_{15}H_{13}N_3S_2$	N : 14.31	14.05
1-phenyl-5-*m*-tolyl-B	5-phenylimino-3-*m*-tolylimino-D	185	80	$C_{15}H_{13}N_3S_2$	N : 14.21 S : 21.05	14.05 21.40
1-phenyl-5-*p*-ethoxyphenyl-B	5-phenylimino-3-*p*-ethoxyphenyl-imino-D	161	72	$C_{16}H_{15}N_3S_2O$	C : 59.63 H : 4.68 N : 12.53	59.71 4.55 12.76
1-phenyl-5-*p*-Cl-phenyl-B	5-phenylimino-3-*p*-Cl-phenyl-imino-D	184-85*	78	$C_{14}H_{10}N_3S_2Cl$	C : 52.71 H : 3.21 N : 13.01	52.58 3.13 13.14
1-phenyl-5-ethyl-B	5-phenylimino-3-ethylimino-D	141	40	$C_{10}H_{11}N_3S_2$	N : 17.51 S : 26.84	17.72 27.01

Where B = 2-S-*p*-Cl-benzyliso-4-thiobiurets and

D = 1,2,4-dithiazolidine.

*R. Singh & V. K. Verma reported m. p. 185° *J. Indian Chem. Soc.*, 1975, Vol. LII, 444.

Typical ir frequencies (cm^{-1}) of 5-phenylimino-3-*m*-tolylimino-1,2,4-dithiazolidine :

Ring-C-S (700 m)[5], C=N (1588 s)[6], ring-S-S-linkage (500 m)[7].

Reduction of 3,5-diaryl/arylalkylimino-1,2,4-dithiazolidines by ethanolic ammoniacal hydrogen sulphide : The dithiazolidines were dissolved in ethanolic ammoniacal hydrogen sulphide and a stream of hydrogen sulphide passed for 20-30 mints. The clear solution on dilution with water or acidification afforded the corresponding dithiobiuret. These were recrystallised from ethanol. The identity of each product was established by observing undepressed mixed melting points with the authentic sample obtained by the reductive de-*p*-Cl-benzylation of the isodithiobiurets (II) with hydrogen sulphide in ethanolic-ammoniacal solution. These were further characterised by superimposable I. R. spectra.

Reductive de-p-Cl-benzylation of 1, 5-diaryl/arylalkyl-2-S-p-Cl-benzyliso-4-thiobiurets by alkaline hydrogen sulphide to the corresponding 2, 4-dithiobiurets : The isodithiobiurets (II) were dissolved in ethanolic solution of sodium sulphide (10 per cent) and a stream of hydrogen sulphide was passed for 3 hrs. The resulting solution on filtration and neutralization with acetic acid yielded the dithiobiurets (III). These were recrystallised from ethanol.

Oxidation of 1,5-diaryl/arylalkyl-2,4-dithiobiurets to the corresponding 3,5-diaryl/arylalkylimino-1,2,4-dithiazolidines : The dithiobiurets (III) were oxidised with bromine in ethanolic solution and on addition of ether the hydrobromides of the respective dithiazolidines precipitated. Free bases were obtained by treating these with ammonia and were recrystallised from ethanol and chlorobenzene. These were found to be identical with the respective 3,5-diaryl/arylalkylimino-1,2,4-dithiazolidines (IV). The identity was further confirmed by ir spectra and mixture melting point technique.

Acknowledgement

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Interaction Between Certain Cations and the Humic Acid Extracted from Different Gujarat Soils

R. K. SHAH, M. R. CHOKSHI* and K. P. SONI

Chemistry Department, University School of Sciences, Gujarat University, Ahmedabad-380009, India

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Humus is a colloidal complex body, the exact nature of which depends on its origin and its mode of formation. The entire fraction of soil humus behaves as colloidal complexes and possesses exchange properties.

The complexes of metal-humic acid were studied potentiometrically in presence of various metal ions like Fe^{+3}, Al^{+3}, Cu^{+2}, Ni^{+2}, Zn^{+2}, Co^{+2}, Mn^{+2} and K^{+}.

The study of properties of humic acid complexes of metal ions can be used in plant nutrition and plant growth study.

SOIL organic matter has long been known to be capable of complexing metals. These complexes influence the availability of the metals to plants[1-4]. Soil organic matter can form stable complexes with metal ions but much remains to be learnt of the mechanisms involved in these reactions. These reactions depend upon the kind and number of functional groups present on the exchange sites[5]. The complex formation of cations with humic acid fraction of soil organic matter is slowly becoming more and more important; since they play a significant role in plant nutrition. It is believed that ion exchange, surface adsorption, chelation and peptization processes are involved in these reactions[6-11].

In this paper, an attempt has been made to study the interaction of certain metallic ions and the extracted humic acids of four different soils of Gujarat. Potentiometric titrations of humic acids in presence of cations were carried out; the titration curves showed the formation of metal-humic acid complexes. Soils selected for the study have different proportions of organic matter; ranging from 1 to 3% (Ahwa-2.91, Junagadh-1.78, Piplod-2.0, Rajkot-1.02). Number of dissociation constants of extracted humic acids of these soils have been found to be two.

Experimental

Humic acids were extracted from different soils of Gujarat (Ahwa, Junagadh, Piplod, Rajkot) by alkali method and were purified by HCl+HF treatment, dialysis and using ion exchange column (Amberlite-IR-120)[12-14]. 0.010 gm of extracted humic acid was taken in 100 ml of double distilled water and 2 ml of 0.02 *M* metal ion solution was added and *p*H titration was carried out using 0.01 *N* NaOH solution. No attempt was made to keep the ionic strength constant. Beckman *p*H meter was used and was standardized with buffers of *p*H 4.0 and *p*H 7.0. A.R. grade chemicals were used for preparation of metal chloride solutions. All solutions used in the above study were prepared in double distilled water. The titrations reading are depicted graphically in Figs 1-3. Tables 1 and 2 present calculation of release of protons (H^+) at *p*H 7.5 and 8.0.

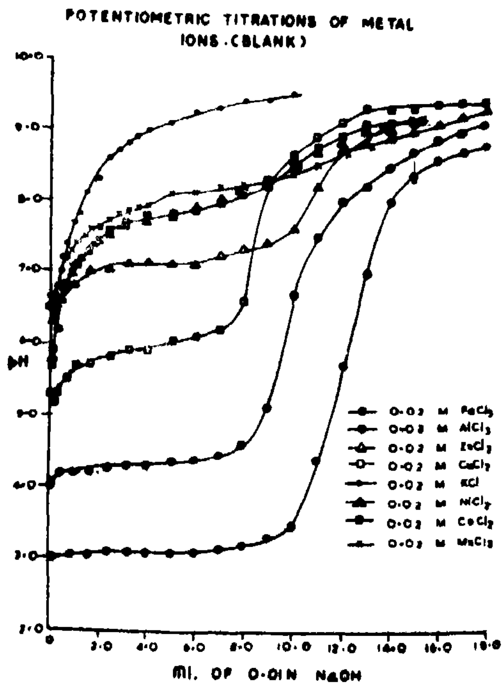


Fig. 1

* Chemistry Department, Bhavan's R. A. College of Science, Ahmedabad-380001.

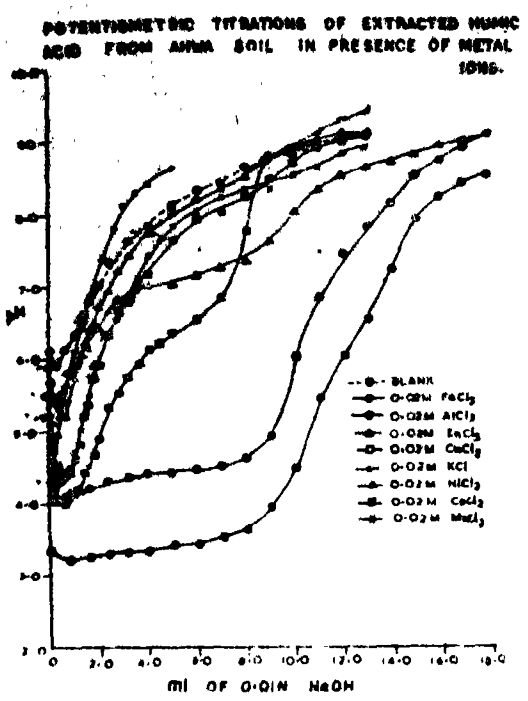


Fig 2.

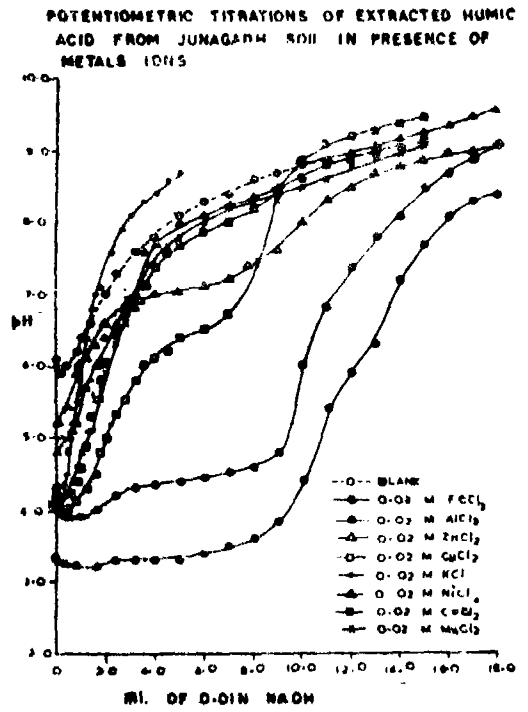


Fig 3.

Discussion

Titrations of the extracted humic acids with metal ions are shown in Figs. 1-3. The formation of metal hydroxides was indicated by the inflections in the titration curves. The basicity of the extracted humic acids can be obtained from the shape of the titration curves. When 2 ml of 0.02 *M* salt solution was titrated, metal-complex formation as well as the precipitation of metal hydroxides occurred in stages.

When the titrant 0.01*N* NaOH solution is added, the following reactions may take place in absence of metal ions as well as in presence of metal ions.

$$H.A + NaOH \rightarrow H_2O + Na^+, A^- \ (A^- - \text{humate})$$

$$n.H.A + M^{n+} + n.NaOH \rightarrow n.H_2O + nNa^+ + MA_n (MA_n - \text{metal humate})$$

From the titration curves of humic acids in presence of metal ions it is found that the curves for Co(II), Ni(II), Mn(II) are very close to each other and there is slight displacement of the titration curves upon the addition of these metals. But in the case of Zn(II), Cu(II), Fe(III), and Al(III), the displacement is high. It is also found that the curve of Zn intersects the curve of Cu(II) at *p*H near about 7.2 to 7.5. This is perhaps, due to the formation of $Zn(ONa)_2$ after *p*H 7.5 [15-16].

Beckwith[7] pointed out that the ability of the metal ions to form complexes with humus substances depends upon the relative *p*H drop on the addition of the respective metal ions to humus substances. Humus substances have the ability to form complexes or chelates with the metal ions because of the presence in their molecules of hydrophillic groups situated inside radicals.

It has been shown that the interactions of metal ions with humic acid causes the displacement of H from some of the functional groups and the formation of complex compounds[6,9,10,17,18]. Release of proton

TABLE 1—CALCULATION OF RELEASE OF PROTONS (H^+) AT *p*H 7.5

Metal ion	Blank	Ahwa	Junagadh	Piplod	Rajkot
Fe^{+3}	3.40	2.85	2.83	2.85	2.75
Al^{+3}	2.75	2.30	2.25	2.40	2.28
Cu^{+2}	2.15	1.23	1.35	1.23	1.68
Zn^{+2}	2.38	1.43	1.35	1.70	1.70
Ni^{+2}	0.55	0.10	0.15	0.15	0.70
Co^{+2}	0.60	0.38	0.25	0.13	0.65
Mn^{+2}	0.35	0.30	0.28	0.10	0.38

TABLE 2—CALCULATION OF RELEASE OF PROTONS (H^+) AT *p*H 8.0

Metal ion	Blank	Ahwa	Junagadh	Piplod	Rajkot
Fe^{+3}	3.50	2.63	2.70	2.75	2.50
Al^{+3}	3.00	2.20	2.15	2.50	2.50
Cu^{+2}	2.23	0.90	0.95	0.95	1.93
Zn^{+2}	2.68	1.33	1.25	1.63	1.75
Ni^{+2}	1.08	0.08	0.13	0.80	1.00
Co^{+2}	1.73	0.58	0.50	0.50	1.00
Mn^{+2}	1.73	0.58	0.25	0.75	0.20

from various metal humic acid complexes were calculated at different pH values ; viz. 7.5 and 8.0 according to Martell and Calvin[19]. Results are given in tables 1 and 2. Theoretically, complete complex formation of divalent cation with humic acids should release 2 protons per mole of the metal ion or cation. On the other hand, the release of protons equivalent to the number released by metal alone would indicate that the complex formation with extracted humic acids did not occur but that basic salts were formed. The number of protons set free per mole of added metal were calculated at pH values of 7.5 and 8.0 from the titration curves (Figs. 1-3). For the calculations, the following equations were employed.

(I) (i) 1000 ml $1N$ NaOH$\equiv$1 gm equivalent of H

(ii) X ml of $0.01N$ NaOH$\equiv$0.001 x X x 0.01

(II) 2 ml of 0.02 M metal added (0.02 M mole) 0.02x2/1000

(III) Number of proton (H^+)

$$= \frac{0.001 \times X \times 0.01}{0.04/1000} \times 4$$

X = difference of 0.01 N NaOH at the particular pH, between (a) metal ion + humic acid, and (b) humic acid alone.

The additional consumption of alkali in the presence of metallic cations was caused by neutralization of protons released from the functional groups of the extracted humic acids. Over the pH range of titrations, the proton release of all the cations (Fe^{+3}, Al^{+3}, Cu^{+2}, Zn^{+2}, Ni^{+2}, Co^{+2}, Mn^{+2})-humic acid complexes never equalled to that of the metal alone (Diags. 1-3). For example, in the presence of one mole of Zn^{+2}, the proton released at pH 8 0 (Table-2) from soils ; Ahwa, Junagadh, Piplod, Rajkot were 1.33, 1.25, 1.63, 1.75 respectively. The corresponding values for Zn^{+2} alone was found to be 2.68. These observations further suggested that the added cations formed complexes with the extracted acids. Over the pH range used in the experiments (pH 7.5 and pH 8.0), the number of protons release did not approach the blank values. Similar remarks may be applied to trivalent cations (Fe^{+3}, Al^{+3}). From the table, it is clear that proton values in the presence of these cations are definitely lower as compared to blank values. However, it may be mentioned that above pH 8.0, hydroxocomplexes of the cations may also be formed. Again in the case of extracted humic acid from Rajkot soil, the discrepancies may be ascribed to the nature of climatic zones (Ahwa, Junagadh and Piplod are classified as forest soils while Rajkot is a semiarid soil).

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Notes

Intake of Calcium and Magnesium by Indian Clay Minerals

P. C. SRIVASTAVA, SHARAFAT ALI and S. K. DE

Department of Chemistry, University of Allahabad, Allahabad.

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CALCIUM and magnesium are well known essential secondary elements that are required by plants for their good growth and development. Since clays and clay minerals are important factors in soils that direct their availability and retention, an attempt has been made in this paper to study the extent of intake of calcium and magnesium from solutions of calcium and magnesium chloride by three important clay minerals viz., kaolinite, illite and bentonite at 20°, 30° and 40°. A search of the literature will show that this aspect of study is yet to be taken up especially with the Indian clay minerals at the three temperatures mentioned earlier.

Experimental

The study of intake of calcium and magnesium was done from their chloride solutions by three pure clay minerals viz., montmorillonite, illite and kaolinite. These clay minerals were identified earlier by X-ray analysis.

For the intake (adsorption) study, 0.25g of the clay minerals taken in 100 ml. volumetric flasks, was treated with the respective solutions (M/25, M/50, M/100, M/200 and M/400) of calcium and magnesium chlorides and the volume was made up by adding the requisite quantity of water. The flasks were kept in a thermostat maintained at a particular temperature (20°, 30° or 40°) and the adsorption experiments were carried out at the required temperatures both for the single and combined ions of calcium and magnesium. The terms "intake" and "adsorption" are used here synonymously.

Results and Discussion

A perusal of table 1 will show that at all the three temperatures, calcium and magnesium intake by bentonite is maximum and there is almost no difference in the values obtained for illite and kaolinite. It is known[1] that of the three clay minerals, mont-morillonite is formed naturally more under conditions where there is good base supply and this condition is not as much required by illite and kaolinite although illite formation does not take place in acidic condition as is required for kaolinite[1]. The structure of montmorillonite therefore develops in a fashion that will have naturally greater capacity for the intake of these two basic ions.

TABLE—1. INTAKE OF CALCIUM AND MAGNESIUM FROM THEIR CHLORIDES IN AQUEOUS MEDIA AT 20°, 30° AND 40°

Clay Minerals	Initial Conc. mg/25 ml		Adsorption (x/m)					
			20°		30°		40°	
	Ca	Mg	Ca	Mg	Ca	Mg	Ca	Mg
	40.08	24.32	37.07	22.61	37.02	22.62	36.96	22.62
	20.04	12.16	18.76	11.36	18.50	11.33	18.50	11.30
Kaolinite	10.02	6.08	9.24	5.64	9.27	5.61	9.24	5.64
	5.01	3.04	4.67	2.84	4.64	2.83	4.64	2.77
	2.50	1.52	2.32	1.41	2.29	1.40	2.32	1.40
	40.08	24.32	37.00	22.62	37.03	22.61	36.98	22.58
	20.04	12.16	18.51	11.30	18.51	11.35	18.51	11.31
Illite	10.02	6.08	9.29	5.66	9.31	5.67	9.28	5.61
	5.01	3.04	4.64	2.83	4.65	2.82	4.63	2.83
	2.50	1.52	2.32	1.42	2.32	1.40	2.32	1.41
	40.08	24.32	37.13	22.69	37.17	22.70	37.17	22.69
	20.04	12.16	18.66	11.43	18.65	11.35	18.63	11.38
Bentonite	10.02	6.08	9.42	5.74	9.39	5.75	9.40	5.71
	5.10	3.04	4.78	2.90	4.75	2.91	4.77	2.90
	2.50	1.52	2.39	1.48	2.38	1.46	2.39	1.47

In presence of each other (table 2), the total intake of calcium and magnesium remains the same when compared with the intake values of calcium and magnesium singly. Under this condition, their combined intake is maximum with bentonite at 20° and at 40° this was maximum with kaolinite.

In general, at all the three temperatures, intake of calcium by the three clay minerals is maximum in comparison to magnesium.

TABLE—2. INTAKE OF Ca+Mg FROM THEIR MIXED CHLORIDE SOLUTIONS AT 20°, 30° AND 40°.

Clay Minerals	Initial Conc. mg./25 ml	Adsorption (x/m)		
		20°	30°	40°
Kaolinite	24.32	22.59	22.62	22.60
	22.16	11.26	11.23	11.33
	6.08	5.61	5.59	5.60
	3.04	2.82	2.80	3.04
	1.52	1.41	1.42	1.50
Illite	24.22	22.63	22.61	22.59
	12.16	11.28	12.09	11.22
	6.08	5.63	5.59	5 57
	3.04	2.81	2.82	2.81
	1.52	1.30	1.40	1.40
Bentonite	24.32	27.77	22.81	23.69
	12.16	11.34	11.31	11.28
	6.08	5.66	5.66	5.63
	3.04	2.87	2.87	2.83
	1.52	1.45	1.46	1.41

The adsorption of calcium and magnesium by the three clay minerals under all conditions appears to be exothermic or their maximum intake is observed to be at 20°. This intake appears to occur in multimolecular layers as their adsorption values do not obey Langmuir's equation of adsorption.

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Lupeol from the seed of *Lycopersicon esculentum*

V. K. SAXENA

Chemistry Department, University of Saugar, Sagar, M.P.

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LYCOSPERSICON esculentum[1] belongs to the family Solanaceae and is rich in Vitamins A and C.

Experimental

Dried and finely powdered seed of *L. esculentum* on extraction with petroleum ether (40 – 60°) in a soxhlet extractor and the extract on concentration (150 ml.) yielded a greenish white deposit (0.9 gm.). The deposit was dissolved in hot methanol and when cooled, a white mass (0.7 gm.) was separated. which on crystallisation yielded a white crystalline compound m. p. 213.5°, C=84.43%, H=11.62%, molecular weight by semi-micro rast=399, molecular formula $C_{30}H_{50}O$, $[\alpha]_D^{s}=27°$ (in $CHCl_3$), m. p. of acetylated derivative 214°, $[\alpha]_D^{s}=47°$ (in $CHCl_3$), m.p. of benzoate derivative=264°. The compound gave positive Salkowsky reaction[2], Libermann—Burchard reaction[3], red colour with Noller's reagent[4], reddish violet colour in Brieskorn test[5], Tischugajen reaction[6] and yellow colour with tetra nitromethane[7] Ruzicka. Thus it is identified as Lupeol. Mixed melting point determination with an authentic sample of *lupeol* also confirmed its identity as *lupeol*.

The identification of this compound is further supported by spectral data, U. V. (Methanol) λmax = 200 mμ I. R. (KBr)=3235 (M), 1640 (W), 1490 (W), 1382 (M), 1185 (W), 1105 (W), 1040 (W), 1 14(W), 985(W), 945(W)cm⁻¹, N.M.R. in $CDCl_3$ using TMS as internal standard, showed signals at 4.64 and 3.18τ.

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Chemical Examination of Stem Cuttings of *Pterospermum heyneanum* Wall

K. P. TIWARI*, R. N. CHOUDHARY and Y. K. SINGH RATHORE

Department of Chemistry, University of Allahabad, Allahabad-211002.

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PLANT. *Pterospermum heyneanum* (N. O. Leguminoseae). *Uses.* medicinal.[1] *Previous work.* Nil. *Present work.* Powdered, air dried stem cuttings were extracted with hot ethanol. The viscous mass obtained on concentration under reduced pressure was then extracted successively with petroleum ether, benzene, ether, ethyl acetate, acetone and methanol. The petroleum ether extract, on concentration, deposited a yellow solid which on chromatography over neutral alumina, followed by preparative T.L.C. yielded a compound, m.p. 136-7°, which was identified as β-sitosterol[2] (m.p., m.m.p., superimposable IR).

The ether extract obtained was concentrated, dried, chromatographed over a column of silica gel. Elution with ethyl acetate, yielded another compound, molecular formula, $C_{15}H_{10}O_6$, m.p. 276-8°. It was

characterised as kaempferol by m.m.p., co-chromatography, microdegradation[3,4] and spectroscopic examinations[5].

Ethyl acetate extract on concentration gave a flavone glycoside, which when purified by column chromatography melted at 268° and analysed for $C_{22}H_{22}O_{11}$. On hydrolysis with mineral acid, it gave an aglycone $C_{16}H_{12}O_6$, m.p. 295°, and glucose. The aglycone has been found to be kaempferide (4'-methyl ether of kaempferol) by analysis, colour reactions, spectral data and preparation of derivatives. The glucose unit has been shown to be linked to 7-hydroxyl group by the study of spectral shift using aluminium chloride[6] and sodium acetate[7]. The presence of glucose in the pyranose form has been proved by periodate oxidation and the presence of a β-glycosidic linkage has been confirmed by its hydrolysis with emulsin. Work on other compounds isolated from *Pterospermum heyneanum* is in progress.

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Study of Thallium (I)-Glycollate, Lactate and Mandelate Complexes.

K. N. SAHU

Chemical Laboratory, Birla Institute of Technology, Mesra, Ranchi,

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THALLOUS complexes with glycollic, lactic and mandelic acids have not been cited in the literature. In the present investigation author has therefore chosen these complexes for the study of their composition and stability.

E. Merck thallous nitrate and B.D.H. (Analar) glycollic, lactic and mandelic acids are used for preparing the solutions in double distilled water. Conductance measurements are done with "DORON" conductivity bridge with 1000 cycle WTW oscillator and dip type conductivity cell. Absorbance measurements are done with the Beckman model DU quartz spectrophotometer using 5 mm light path absorption cells. All measurements are carried out at a temperature of 28 ± 0.5° and at a *p*H of 6.5.

The composition of the complexes are first studied by monovariation[1] method. 0.033*M* and 0.025*M* equimolar solutions were mixed keeping the volume of metal solution as 5ml and varying the volume of ligand solution making total volume equal in all the cases. Thallous ion forms 1 : 1 complexes with all the three ligands. The composition was further confirmed by Job's method[2] using conductance and absorbance as index properties. For conductance measurement 0.025*M*, 0.012*M* and for absorbance 0.05*M* equimolar solutions were employed.

The instability constant and hence the stability constant of the complexes are determined by Job's method[2]. For conductance measurement 'P' (Molar concentration of ligand/Molar concentration of metal solution) was kept at 1.5, 2.0 and 2.5 with C = 0.01*M*. For spectrophotometric study 0.02 *M* metal and 0.05*M* ligand solutions were mixed, and for each ligand readings were recorded at three different wave lengths according to suitability ranging from 245 to 280 nm.

The values of dissociation constants both by conductometric and spectrophotometric methods are in good agreement with each other and are reported to be 2.11×10^{-2}, 9.22×10^{-2} and 11.7×10^{-2} respectively for the thallous glycollate, -lactate and -mandelate complexes.

The change in the free energy of formation of glycollate, lactate and mandelate complexes by the equation $F = -RT \ln K$ are calculated to be −2.299, −1.421 and −1.279 K. cals per mole respectively at 28°.

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Titrimetric Determination of Copper(II) with Thioglycollic Acid.

SAMEER BOSE, M. P. SAHASRABUDDHEY
and
KRISHNA K. VERMA

Department of Chemistry, Government Science College, University of Jabalpur, Jabalpur 482001.

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A method for the determination of copper(II) in aqueous solution is described based on the titration of a cupric salt solution with standard thioglycollic acid solution. Cupric ion oxidises thioglycollic acid to dithioglycollic acid with the simultaneous formation of cuprous mercaptide[1,2]. The latter compound

complexes excess cupric ion leading to the formation of a mixed cuprous-cupric mercaptide which in the present case is violet. On adding thioglycollic acid the mixed mercaptide breaks and at the end point the violet colour is replaced by a permanent yellow precipitate of cuprous mercaptide. The overall process is represented by the following equation,

$$2\ Cu^{2+} + 4\ HSCH_2CO_2H \rightarrow 2\ CuSCH_2CO_2H + (-SCH_2CO_2H)_2 + 4H^+$$

Although iodometry is a common procedure for the determination of copper(II), the method is vitiated by the presence of compounds that react with iodine liberated on adding potassium iodide to copper(II) salt solution. The thioglycollic acid method can tolerate a number of such compounds. No indicator is required for titration and the thioglycollic acid solution is to be checked only after each two weeks.

Experimental

Reagents: A $0.05M$ solution of copper(II) sulphate was prepared by dissolving a right amount of AnalaR sample in distilled water. Its strength was checked by iodometric titration. Less concentrated solutions were made by appropriate dilution.

An aqueous solution of $0.1M$ thioglycollic acid was prepared by dissolving an approximate volume of 98-99% pure sample. Its strength was determined by oxidising with a known excess of iodine solution followed by titrating the latter with standard thiosulphate[3]. Alternatively and if the same burette is to be used for filling thioglycollic acid, the following method may be used.

In a 150-ml Erlenmeyer flask 10 ml of 0.1 *N* iodate solution is taken and treated with 0.5g of potassium iodide plus 3ml of $1M$ sulphuric acid. The liberated iodine is diluted with 25ml of distilled water and titrated with thioglycollic acid being delivered from a 10-ml burette graduated in 0.02 ml. About 1 ml of 0.5% starch is added only when the solution of the flask is yellow and the blue complex is further titrated to colourless end point. The following reaction occurs

$$2\ HSCH_2CO_2H + I_2 \rightarrow (-SCH_2CO_2H)_2 + 2HI$$

Procedure: A measured volume (about 10-30ml) of copper(II) salt solution (containing about 6-50mg of copper) is taken in a 150-ml Erlenmeyer flask. A $0.05M$ solution of thioglycollic acid is used, when the sample solution contains upto 23mg of copper and a $0.1M$ titrant for higher amounts. The contents of the flask are swirled regularly during titration. At the end point the deep violet complex first formed changes to a permanent yellow. Near the end-point the titrant is added slowly with vigorous shaking.

Results

Copper(II) salt with sulphate, nitrate, chloride or acetate may be directly titrated with thioglycollic acid. A pH of 4 is best suited for the titration. In the case of copper(II) acetate the desired pH may be brought down by dropwise addition of dilute hydrochloric acid. Results for the determination of copper(II) are given in Table 1. It follows from the equation for the reaction of copper(II) with thioglycollic acid that 1ml of $0.05M$ thioglycollic acid is equivalent to 1.5885 mg of copper. The proposed method is accurate to 0.3% with a standard deviation of 0.2‰. Cinnamic acid, sodium formate, allylalcohol, glycine, cystine and zinc, bromide, chloride and sulphite ions can be tolerated. Serious interference is caused by iron(III), lead(II), tin(II), silver(I) and mercury(II) ions.

TABLE—1. DETERMINATION OF COPPER WITH THIOGLYCOLLIC ACID

Copper (mg) Taken	Found	± Diff. (mg)
6.40	6.39	− 0.01
12.80	12.72	− 0.08
18.55	18.50	− 0.05
25.60	25.52	− 0.08
30.42	30.49	+ 0.07
36.56	36.46	− 0.10
44.61	44.72	+ 0.11
50.80	51.06	+ 0.26

Acknowledgement

Sincere thanks are due to Dr. G. S. Lamba, Head, Department of Chemistry and to Dr. M. G. Nene, Principal, Government Science College, Jabalpur, for providing research facilities.

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Spectrophotometric Determination of Mercury(II) with Cyclopentanone-2-carboxyanilide

SANAT KUMAR MANDAL and JYOTIRMOY DAS

Department of Chemistry, The University of Burdwan, Burdwan, West Bengal.

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SEVERAL β-ketoanilides have been recommended for the gravimetric determination of mercury(II)[1-3]. This report describes the use of cyclopentanone-2-carboxyanilide as a reagent for the extraction spectrophotometric determination of mercury(II).

Experimental

Chemicals and reagents : Cyclopentanone-2-carboxyanilide was prepared in the laboratory[4] and pure mercury(II) nitrate (E. Merck) was used. A citrate buffer of *p*H 6.5 was prepared from 1g of citric acid (G. R., E. Merck) and sodium hydroxide. A Hilger and Watts H700 Uvispek spectrophotometer was used.

Procedure : Add 1ml of the stock citrate buffer to mercury(II) solution containing 50-450 μg of the metal, dilute to 10 ml, heat to 50° and add 50-60 mg of cyclopentanone-2-carboxyanilide dissolved in 3-4 ml of ethanol. Adjust the *p*H to 6.2-8.0 with 2*N* sodium hydroxide solution, cool and extract the complex with two 5 ml portions of isobutyl methyl ketone. Dehydrate the combined extract with sodium sulphate and measure the absorbance at 345 nm against pure solvent within three days.

Results and Discussion

The wave-length of maximum absorbance for the mercury(II) complex was 345 nm where the reagent showed no absorption and Beer's law was valid upto 45 μg of mercury per ml of the solvent.

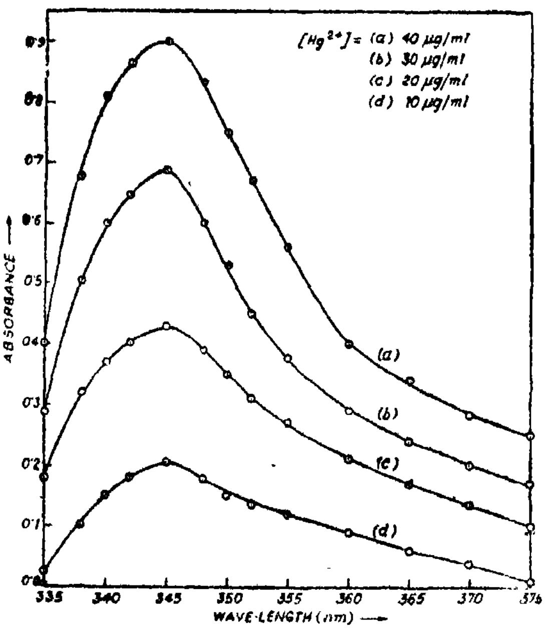


Fig. 1. Absorbance Curves of Hg (II)-Cyclopentanone-z-Carboxyanilide in isobutylmethyl Ketone.

The complex was extracted in chloroform, benzene and carbon tetrachloride with difficulty. Isobutylmethyl ketone was selected as the extracting solvent due to ease in extraction and the stability of the complex. Approximately 96% of the complex was recovered by one extraction. About 50-60 mg of the reagent was sufficient provided the complex was allowed to form before extraction. Larger amounts of it were required when the extraction was tried with cyclopentanone-2-carboxyanilide dissolved in the ketone.

Extraction was quantitative above a *p*H of 6.2. However, mercury(II) (300 μg) could be determined with a relative standard deviation of ±1%, in the presence of 0.[illegible]0 mg of Cu(II), Cd(II), Co(II), Ni(II), Zn(II), Fe(III) or Al(III) provided the *p*H was adjusted to 7.0-7.5.

Mole-ratio and slope-ratio methods indicated the formation of a mercury(II) bis-complex, the dissociation constant being 5.97×10^{-15}. The Sandell sensitivity was 4.6×10^{-3} μg of mercury(II) per cm^2 while the molar absorptivity at 345 nm was 4400±4%.

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Molecular Interactions – Studies on the Distribution of Aniline between Water and Binary Mixtures of Organic Solvents*

K. GANAPATHY

Department of Chemistry, Annamalai University, Annamalainagar

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THE distribution coefficients of aniline between water and binary mixtures composed of different weight fractions of carbon tetrachloride with benzene or nitrobenzene have been measured at 30° and 40°. The changes in the thermodynamic parameters of free energy, enthalpy and entropy accompanying the transfer of one mole of aniline from the aqueous layer to the organic layer have been calculated.

Experimental

All the chemicals used in the present investigation were of Analar quality. The organic liquids were purified by the usual procedures[1]. Double-distilled water was employed. The weight percentages of the organic solvents in the binary solvent mixtures were calculated from the known volumes of the two solvents and their density values at 30°.

The method adopted for the determination of the distribution coefficient was the conventional one[2]. The initial concentration of aniline in the aqueous layer was kept at 0.01 *M* in all the experiments. In order to

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bring the systems effectively into equilibrium in each case, the mixture of the organic solvents or the pure organic solvent and the aqueous solution of aniline were kept in the thermostat at the desired temperature and mechanically agitated for about an hour using a mercury-sealed stirrer to prevent evaporation of the solvents. After the two layers separated, each was analysed for its aniline content by the Winkler method[9].

Results and Discussion

The distribution coefficients reported refer to the following equilibrium :

Aniline (water) ⇌ Aniline (organic solvent)

for which $K_{dist.} = \frac{[\text{Aniline in the organic layer}]}{[\text{Aniline in the aqueous layer}]}$

The enthalpy change ($\triangle H^\circ$) of the forward process was calculated using the integrated form of the van't Hoff equation :

$$\frac{d \ln K_{dist.}}{dT} = \frac{\triangle H^\circ}{RT^2}$$

The free energy change ($\triangle G^\circ$) and the entropy change ($\triangle S^\circ$) at the two temperatures were obtained from the following equations:

$$\triangle G^\circ = -RT \ln K_{dist.}$$

$$\triangle S^\circ = \frac{\triangle H^\circ - \triangle G^\circ}{T}$$

The data are given in Table 1 and Table 2.

A survey of the data reveals the following facts :

(i) The transfer of one mole of aniline from the water layer to the nitrobenzene layer is exothermic but is endothermic with the other two solvents, carbon tetrachloride and benzene.

(ii) In all cases $\triangle G^\circ$ decreases with increase of temperature.

(iii) The $\triangle S^\circ$ values are all positive and do not change with temperature. With different organic solvents, the value increases in the order nitrobenzene < carbon tetrachloride < benzene (4.98, 6.20 and 7.27 e.u. mole^{-1} respectively).

TABLE—1. DISTRIBUTION COEFFICIENTS OF ANILINE BETWEEN CARBON TETRACHLORIDE-NITROBENZENE MIXTURES AND WATER, AND RELATED THERMODYNAMIC PROPERTIES

Mole % of carbon tetra-chloride	K_{dist} 30°	K_{dist} 40°	$-\triangle G^\circ$ Calories mole^{-1} 30°	$-\triangle G^\circ$ Calories mole^{-1} 40°	$\triangle H^\circ$ Calories mole^{-1}	$\triangle S^\circ$ observed e. u. mole^{-1} 30°	$\triangle S^\circ$ observed e. u. mole^{-1} 40°	$\triangle S^\circ$ Calcd. e.u. mole^{-1} 40°	$\triangle\triangle S^\circ$ e.u. mole^{-1}
100	4.11	4.34	850	910	1030	6.20	6.20	—	—
70	10.23	10.46	1400	1460	420	6.01	6.01	5.83	+0.18
51	15.22	15.33	1640	1700	140	5.87	5.88	5.60	+0.28
26	19.17	19.01	1780	1830	−155	5.36	5.35	5.30	+0.05
0	21.67	21.29	1850	1900	−340	4.98	4.98	—	—

TABLE—2. DISTRIBUTION COEFFICIENTS OF ANILINE BETWEEN CARBON TETRACHLORIDE-BENZENE MIXTURES AND WATER, AND RELATED THERMODYNAMIC PROPERTIES.

Mole % of carbon tetra-chloride	$K_{dist.}$ 30°	$K_{dist.}$ 40°	$-\triangle G^\circ$ Calories mole^{-1} 30°	$-\triangle G^\circ$ Calories mole^{-1} 40°	$\triangle H^\circ$ Calories mole^{-1}	$\triangle S^\circ$ observed e. u. mole^{-1} 30°	$\triangle S^\circ$ observed e. u. mole^{-1} 40°	$\triangle S^\circ$ Calcd. e.u. mole^{-1} 40°	$\triangle\triangle S^\circ$ e.u. mole^{-1}
100	4.11	4.34	850	910	1030	6.20	6.20	—	—
85	5.61	5.88	1040	1100	885	6.35	6.34	6.36	−0.02
48	7.13	7.45	1180	1250	830	6.63	6.64	6.76	−0.12
32	8.14	8.50	1260	1330	815	6.85	6.85	6.93	−0.08
15	9.50	9.90	1355	1425	775	7.03	7.03	7.11	−0.08
0	10.98	11.43	1440	1515	760	7.26	7.27	—	—

The more negative $\triangle G°$ values at the higher temperature show that the transfer of aniline from water to the organic layer occurs more readily at elevated temperatures.

The positive values of $\triangle S°$ indicate that the transfer of aniline from water layer to the organic layer results in a greater randomness in orientation of aniline molecules with the organic solvent molecules. This is obviously due to the highly polar nature of water molecules resulting in a greater order in the intermolecular orientation of polar aniline with them than with non-polar carbon tetrachloride and benzene molecules. Since nitrobenzene is the most polar among the three liquids studied, the $\triangle S°$ value is the least with it.

Even though carbon tetrachloride and benzene are both classified as non-polar, the C-Cl bond in the former is more polarisable than the C-H bond in the latter. Hence the possibility of a greater order in the intermolecular orientation of aniline with carbon tetrachloride than with benzene cannot be ruled out. This is confirmed by the greater $\triangle S°$ value with benzene (7.27 e.u.) than with carbon tetrachloride (6.20 e u.).

The $\triangle\triangle S°$ values obtained with mixtures of the two pairs of the organic solvents (Table 1 and Table 2) show that the carbon tetrachloride-nitrobenzene system exhibits a positive deviation from ideal behaviour (i.e. from the simple mixture rule) while with the carbon-tetrachloride-benzene system the deviation is negative. Further the deviation, positive or negative, appears to be maximum at about 50% composition. This might be due to the greater orderly intermolecular orientation among molecules of carbon tetrachloride and nitrobenzene than among molecules of carbon tetrachloride and benzene. Under such circumstances when aniline molecules get transferred from water to the carbon tetrachloride-nitrobenzene mixture a slightly more randomness of orientaiion results than there would be if the systems were ideal.

Acknowledgement

The auth>r thanks Professor V. Baliah, Vice-Chancellor, Nagarjuna University, Guntur for helpful suggestions.

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Condensation of *o*-Phenylenediamine with Ethyl Acetoacetate in presence of Polyphosphoric acid

(Mrs) K. C. DESAI and C. M. DESAI

P. T. Sarvajanik College of Science, Surat

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ETHYL acetoacetate gives with the diamine under acid condition ethyl β-2-amino-anilinocrotonate (m.p. 59°) which undergoes isomerisation to the stable form after eight days (m. p. 85°) in the presence of light ; [1,2,3] in the present work such a *cis-trans* interconversion could be brought about by treatment with boiling water. Sexton[1] obtained in such a condensation a seven-membered ring compound(I) in neutral boiling Xylene ; benziminazole-2-acetone(II) in alkaline condition and 2-methyl-benziminazole(III) by heating the crotonate alone at 100°.

He concluded that (I) or (II) might have been formed from the intermediate, acetoacet-*o*-aminoanilide(IV) which he, however, could not isolate.

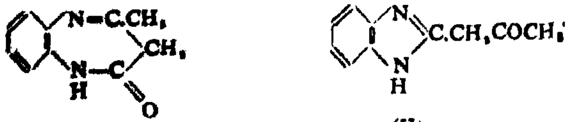
In the present work such a condensation gave with polyphosphoric acid the above four products but each under different experimental condition. It was however observed in numerous experiments that benziminazole-2-acetone was obtained at temperatures 120-140° as a stable product and acetoacet-*o*-aminoanilide at 100° under controlled condition ; its benzene solution on boiling gave benziminazole-2-acetone. The variation in the nature of products obtained may be explained on the basis of the exceptional nature of the reagent[4] and the functional multiplicity of the β-keto ester and diamine.

Experimental

Seven-Membered Ring Compound (*I*) : Freshly prepared polyphosphoric acid (12. ml ; 20 g.) was slowly added to an externally ice-cooled mixture of the diamine (5.4g.) and the keto ester (6.8 ml). The reaction mass was heated to 85° and then kept for 24 hours. It was then heated to 150°, treated with ice and neutralised giving a product which was crystallised from alcohol (m.p. 120° – 121°). Its mixed m.p. with the product obtained by the method of Sexton did not show any depression,

Benziminzole-2-acetone (*II*) : The mixture of the diamine(5.4g.) with the β-ketoester(7 ml.) was mixed with freshly prepared warm PPA (12ml ; 20g.), when a vigorous reaction set in with effervescence. It was heated to 150° and kept at this temperature for ½ hour. Neutralisation in presence of ice with sodium and ammonium hydroxide solutions precipitated a product. Needles from water (2.92g, m.p. 148°), lit.[2] m.p. 148°.

2-Methyl-benziminazole (III) : Hot PPA (12ml ; 20g.) was added to a reaction mass of the diamine (5.4g.) and the β-ketoester (7.0ml) containing a drop of concentrated hydrochloric acid. Turbid layer, separated during reaction, disappeared on stirring. The reaction mass was stirred at 120-130° for 2½ hours. It was treated with ice and just neutralised ; the product (3.2g.) was crystallised from hot water ; m. p. 175° ; its mixed m.p. with the authentic specimen of 2-methyl-benziminazole was undepressed.



(I) (II)



(III) (IV)

Acetoacet-o-aminoanilide(IV) : *o*-Phenylenediamine(5.4g) was added to a solution of orthophosphoric acid (12 ml) containing β-ketoester (6.8 ml), externally cooled with ice ; phosphorous pentoxide(20g) was added to this solution in small lots ; the mixture was then heated on steam-bath for ½ hour. The reaction mass was treated with ice and neutralised with ammonium and sodium hydroxide giving yellow product. Yellow needles from aqueous ethanol (2.68g ; m.p. 105° dec).

Analysis : $C_{10}H_{12}O_2N_2$	requires	N, 14.58%
	found	N, 14.50%

It coupled with diazotised amines giving deep red colour; its benzene solution on boiling gave benziminazole-2-acetone (m.p. 1 ·8°).

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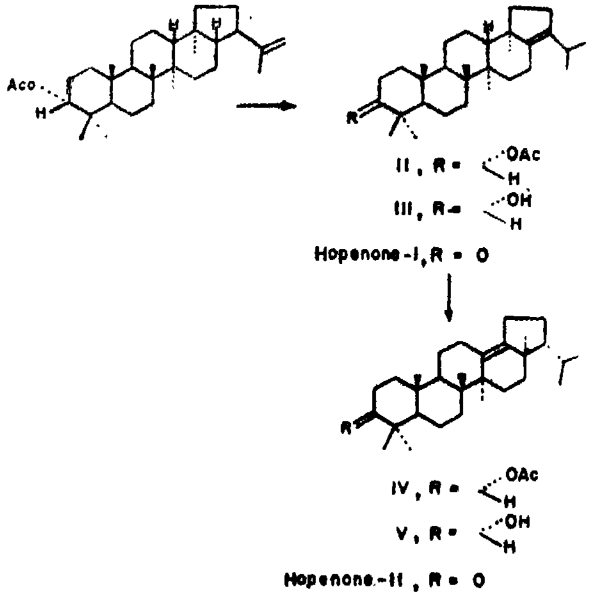
Acid Catalysed Isomerisation of 3-Epi-Moretenyl Acetate

H. N. KHASTGIR* and B. P. PRADHAN

Department of Chemistry, University of North Bengal, Dt. Darjeeling

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3-EPI-MORETENYL acetate[1] (I) on acid isomerisation under mild condition of Fazakerley and co-workers[2] (AcOH-H_2SO_4) furnished hop-17(21)-en-3α-yl acetate (II), m. p. 222-23°, $[\alpha]_D$ + 11.1°. The acetate (II) on hydrolysis (Methanolic-KOH) gave the corresponding alcohol-hop-17(21)-en-3α-ol[3,4] (III), m. p. 185-86°, $[\alpha]_D$+47° which on oxidation with CrO_3-Py complex yielded hopenone-I (identified by m. m. p and IR comparison with an authentic sample prepared from moretenone[1]). The alcohol (III) was also prepared from hopenone-I by Meerwein-Pondorff reduction[5] and was found to be identical (m. m. p. and IR).



Hop-17(21)-en-3α-yl acetate on further isomerisation under strong acid condition of Fazakerley and co-workers[2] (AcOH-C_6H_6-H_2SO_4) yielded an acetate, hop-13(18)-en-3α-yl acetate, (IV), m. p. 179-81°, $[\alpha]_D$ -32 1°, which on hydrolysis (Methanolic-KOH) furnished the alcohol, hop-13(18)-en-3α-ol, (V), m.p. 219-21°,$[\alpha]_D$-14·8°. Oxidation (CrO_3-Py) of the alcohol(V) furnished a ketone, m. p. 148-50°, $[\alpha]_D$ 49°, identical with hopenone-II (m m. p). Meerwein-Pondorff reduction[5] of Hopenone-II yielded an alcohol which was found to be identical with the alcohol (V) and its acetate with (IV) (m.m.p).

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Synthesis and Nucleophilic Addition to Conjugated Imines of 3, 5-Dimethyl-1-(p-anilino)pyrazole

P. S. FERNANDES, N. N. JOSHI, A. J. MENEZES, V. D'SOUZA and V. V. NADKARNY

Nadkarny-Sacasa Research Laboratory, St. Xavier's College, Bombay-1

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IN continuation of our previous work on pyrazole derivatives[1,2], we have now extended the work to study nucleophilic addition on conjugated imines. Recently the synthesis and nucleophilic addition reactions on conjugated imines have been reported[3].

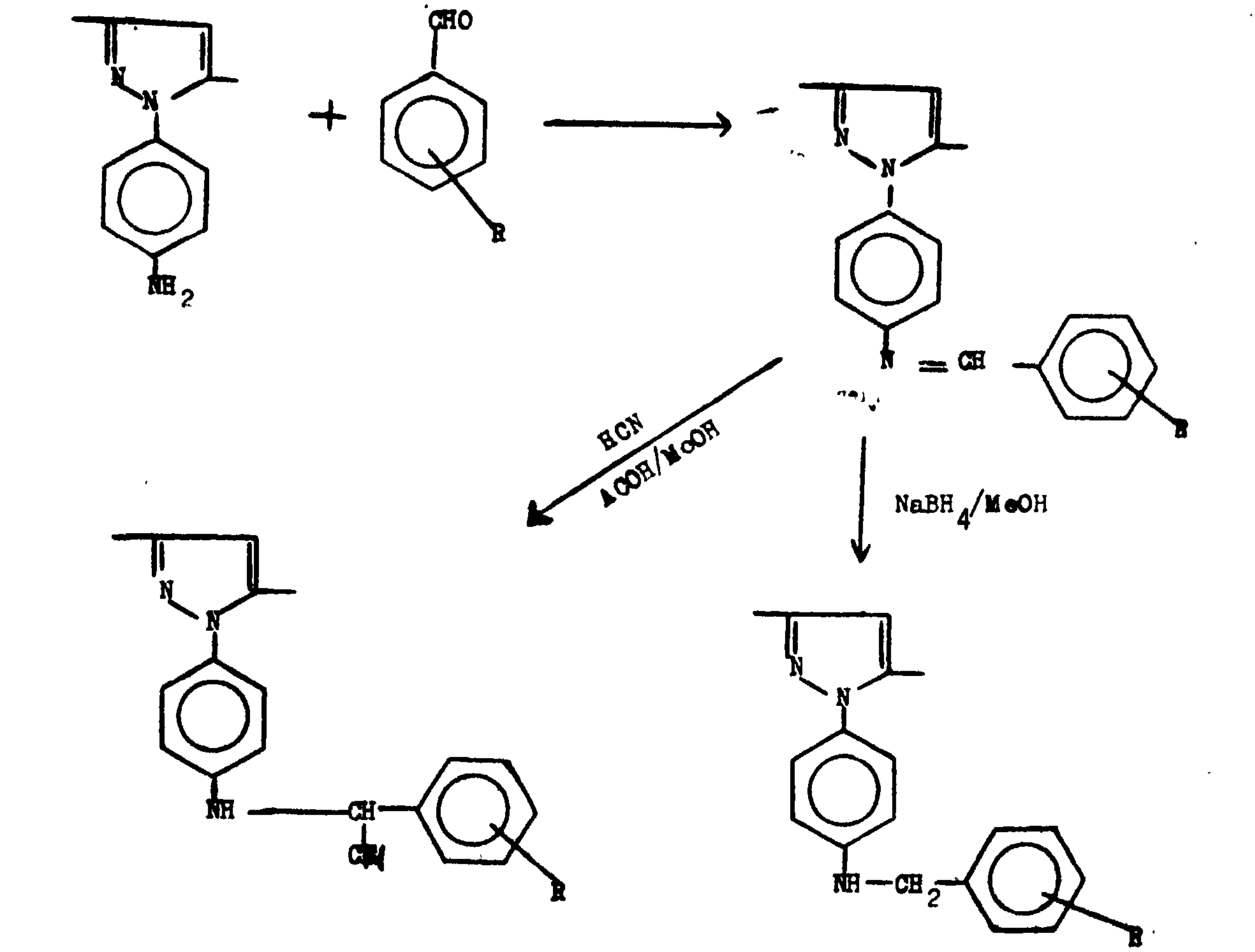
The present communication deals with the synthesis of few imines from 3, 5-dimethyl-1-(*p*-anilion) pyrazole[4] (Scheme I). The imines (I) gave good yields of cyanoimines (II) on treatment with potassium cyanide and acetic acid. The imines (I) were reduced to the dihydro product (III) by sodium borohydride in methanol.

Experimental

3, 5-Dimethyl-1-(*p*-anilino) pyrazole required was synthesised by the method reported in the thesis[4]. The IR spectrum (KBr) showed the absorption for -CH=N- from 1540-1595 cm^{-1}. The cyano imines showed the absorption at 3430 cm^{-1} (-NH-) and 2245 cm^{-1} (-C≡N). The dihydroproducts (III) showed the absorption 3250 – 3300 cm^{-1} for -NH-. The nitro substituted derivative showed the absorption at 1520 cm^{-1} which is characteristic of NO_2 absorption indicating the presence of NO_2. The NO_2 group does not undergo reduction during the reaction with borohydride.

Preparation of imines I (*table 1*) : 3, 5-Dimethyl-1-(*p*-anilino) pyrazole (0.01 mole) was dissolved in ethanol containing few drops of acetic acid, to which was added the appropriate aryl aldehydes (0.01 mole) in ethanol. The mixture was refluxed for 2 hrs. The product separated on cooling was filtered and crystallised from ethanol. Yield 60-80%.

Addition of HCN-imines (*table-2*) : The imines (I) 0.01 mole was dissolved in methanol and the solution was made acidic with acetic acid. A solution of pota-



II

III

Scheme I

TABLE 1

Sr. No.	R	M.P.	Mol. formula	Analysis % Calc. C	H	N	Found C	H	N
1	2-OH	75	$C_{18}H_{17}N_3O$	74.23	5.84	14.43	74.08	5.81	14.14
2	4-OH	210	$C_{18}H_{17}N_3O$	74.23	5.84	14.43	74.14	5.76	14.21
3	4-OCH_3	124	$C_{19}H_{19}N_3O$	74.74	6.23	13.77	74.58	6.26	13.56
4	4-N_2O	155	$C_{18}H_{16}N_4O_2$	67.51	5.00	17.50	67.46	4.93	17.33

ssium cyanide (0.01 mole) in 10 ml water was added to the imine solution with continuous stirring at 0-5°. The precipitate (II) obtained was filtered and recrystallised from methanol. Other nitriles were prepared in an analogous way. Yield 70-80%.

TABLE 2

S. No.	R	M.P. °C	Mol. formula	Analysis % N Calc.	Found
5	2-OH	133	$C_{19}H_{18}N_4O$	17.61	17.42
6	4-OH	220	$C_{19}H_{18}N_4O$	17.61	17.65
7	4-OCH_3	162	$C_{20}H_{20}N_4O$	16.90	16.71
8	4-NO_2	145	$C_{19}H_{17}N_5O_2$	20.17	20.09

Reduction of imines with $NaBH_4$(Table-3): Sodium borohydride (0.03 mole) was added to a methanolic solution of the imine (0.02 mole) over a period of ½ hour at 5-10°. After which the reaction mixture was allowed to stand overnight at room temperature. The excess of sodium borohydride was destroyed by the addition of water and the product was obtained by extraction with ether. The ether extract was washed with water until neutral, dried over anhydrous sodium sulfate and evaporated. The compound (III) thus obtained was recrystallised from methanol. Other dihydrocompounds were obtained in a similar manner. Yield 55-62%.

TABLE 3

S. No.	R	M.P.	Mol. formula	Analysis % N Calc.	Found
9	2-OH	140	$C_{18}H_{19}N_3O$	14.34	14.19
10	4-OH	156	$C_{18}H_{19}N_3O$	14.34	14.14
11	4-OCH_3	110	$C_{19}H_{21}N_3O$	13.67	13.56
12	4-NO_2	113	$C_{18}H_{18}N_4O_2$	17.39	17.31

Acknowledgement

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Chemical Constituents of *Aconitum violacium* and *Polygonum tomentosum*

K. P. TIWARI* and MOHAMMAD MASOOD

Department of Chemistry, University of Allahabad, Allahabad.

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ACONITUM (N. O. Ranunculaceae) is a large genera widely distributed throughout the Northern temperate regions. These are highly poisonous and *most valuable* medicinal plants[1]. The literature survey of the genus *Aconitum* has revealed it to be a rich source of alkaloids[2-6].

The air dried powdered roots (1 kg) were defatted with petroleum ether and then exhaustively extracted with ethanol. The ethanolic extract was concentrated to viscous mass, dissolved in acidulated water (1%HCl), the resulting solution basified with sodium carbonate and then extracted with chloroform. The aqueous solution left after the extraction with chloroform gave positive Molisch's test for the presence of sugars which were identified as glucose and rhamnose by co-chromatographic studies with authentic samples.

The chloroform extract on concentration gave a colourless solid mass which was purified by dissolving it in methanol and reprecipitating with water. The

white mass so obtained was recrystallised from ethanol as white crystals, $C_{36}H_{51}O_{11}$ (m/e 673), m.p. 112-14°, acetyl derivative, m.p. 196-98°. It was characterized as bikhaconitine by co-tlc; m.m.p. and superimposable I.R.[7] with the authentic sample.

Polygonum is a large genera, cosmopolitan but distributed especially throughout the temperate regions. The drug finds extensive uses in medicine[8]. The literature survey of the genus *Polygonum* shows that it is a rich source of flavonoids[9-13].

The air dried powdered plant (4 kg) was extracted with hot ethanol. The ethanolic extract was concentrated under reduced pressure and the thick viscous mass so obtained was refluxed for several times with petroleum ether to remove chlorophyll and fats. The residual mass was extracted with acetone. The acetone extract after concentration under reduced pressure was extracted with ether. The ethereal extract was concentrated and then chromatographed over a column of magnesol[14]. On eluting with ethyl-acetate saturated with water two compounds, A and B, were obtained.

Compound A crystallised from a mixture of acetone: methanol (1:1) as light yellow crystals, $C_{15}H_{10}O_7$ (m/e 302), m.p. 316°, formed an acetate, $C_{25}H_{20}O_{12}$, m.p. 198-99°, O-CH_3 derivative $C_{20}H_{20}O_7$ (m/e 372), m.p. 145-46°. It was characterised as quercetin by comparison of m.p. and I.R[15] with those of authentic sample of quercerin.

Compound B crystallised from methanol as yellow crystals, $C_{16}H_{12}O_7$ (m/e 316), m.p. 294-96°(d.), formed an acetate, m.p. 184-86°, co-tlc, m.m.p. and superimposable IR[15] confirmed its identity with authentic rhamnetin.

The residual acetone extract (left after extraction with ether) was chromatographed over a magnesol column and eluted with ethyl acetate saturated with water, when two flavonoids, C and D were obtained.

Flavonoid C crystallised from methanol as yellow crystals, $C_{21}H_{20}O_{11}$, m.p. 185-87°, gave positive Molisch's test indicating it to be a glycoside. The compound on hydrolysis with 7% sulphuric acid gave quercetin and rhamnose. Co-chromatographic examination and m.m.p. with authentic sample showed it to be quercitrin.

Flavonoid D crystallised from methanol as yellow crystals, $C_{27}H_{30}O_{16}$, m.p. 210-12°. On hydrolyis with 7% sulphuric acid it gave quercetin, glucose and rhamnose and on partial hydrolysis with formic acid[16], quercetin-3-*o*-β-glucoside and rhamnose were obtained. Its identity with rutin was established by m.m.p. with the authentic sample.

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The authors are grateful to Dr. D. S. Bhakuni, Central Drug Research Institute, Lucknow and Dr. T.R. Govindachari, CIBA-GEIGY Research Centre, Bombay for their kind help in the spectral studies of the compounds reported by the authors.

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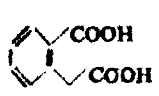
3-Arylisocoumarin : Synthesis of 3-(2′,4′-Dihydroxyphenyl)- ; 3-(2′-methyl-, 4′-hydroxyphenyl)- ; and 3-(3′-methyl-, 4′-hydroxyphenyl)-isocoumarins.

B. K. SARKHEL and JAGDISH N. SRIVASTAVA*

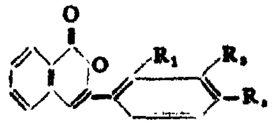
Department of Chemistry, Bhagalpur University, Bhagalpur-812007.

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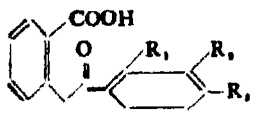
IN continuation of our previous work[1], we report here the condensation of resorcinol, *m*-cresol and *o*-cresol with homophthalic anhydride or acid (I) in the presence of polyphosphoric acid which furnished the corresponding 3-phenylisocoumarin derivatives(II) in 50% yields. These isocoumarin derivatives were subjected to different reactions, e.g. alkaline hydrolysis



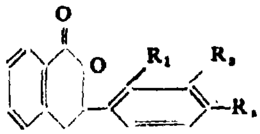
I



II



III



IV

a. $R_1 - R_3 - OH$

b. $R_1 = OH, R_2 = CH_3, R_3 = H$

c. $R_3 = OH, R_2 = CH_3, R_1 = H$

of (II) gave (III) which on reduction with sodium-borohydride yielded (IV). Treatment of (IV) with N-bromosuccinimide followed by dehydrobromination with pyridine gave the original isocoumarin back.

All the above isocoumarins (II) gave fugitive yellow to red colourations possibly due to intermediate quinone structures. (IIIa) was dehydrated at 205° to give back the original isocoumarin.

TABLE—1. 3-ARYLISOCOUMARINS (III)

Aryl Substituent	Formula	M. P. in °C	KBr in cm⁻¹ λ_{max}	MeoH in nm. λ_{max}
2,4-Dihydroxyphenyl.	$C_{15}H_{10}O_4$	226-27 (Lit[1] m.p. 227°)	1710, 1620	315, 270
2-Methyl, 4-Hydroxyphenyl.	$C_{16}H_{12}O_3$	215-16° (Lit[1] m.p. 216°)	3200, 1710, 1620	318, 298
3-Methyl-,4-Hydroxyphenyl.	$C_{16}H_{12}O_3$	232° (Lit[1] m.p 232°)	3250, 1710, 1620, 1600	310, 260

TABLE—2. W-(2′-CARBOXYPHENYL) ACETOPHENONES

Aryl Substituent of the acetophenone	Formula	M.P. in °C	KBr in cm⁻¹ λ_{max}	MeoH in nm. λ_{max}
2,4-Dihydroxy	$C_{15}H_{12}O_5$	—	3200, 1680, 1510.	275
2-Methyl, 4-Hydroxy	$C_{16}H_{14}O_4$	163° (Lit[1] m.p. 163°	3200, 1680, 1510.	275.
3-Methyl, 4-Hydroxy	$C_{16}H_{14}O_4$	210-11° (Lit[1] m.p. 212°)	3250, 1650, 1500.	270.

TABLE—3. 3-ARYL-3,4-DIHYDROISOCOUMARINS

Aryl Substituent	M.P. in °C	KBr in cm⁻¹ λ_{max}	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
2,4-Dihydroxyphenyl	199-201	3290, 1700	70.39	4.7	$C_{15}H_{12}O_4$	70.31	4.69
2-Methyl,4-Hydroxyphenyl.	163-65	3200, 1710	75.50	5.5	$C_{16}H_{14}O_3$	75.48	5.54
3-Methyl,4-hydroxyphenyl.	156-57	3250, 1710	75.50	5.6	$C_{16}H_{14}O_3$	75.48	5.54

Experimental

Melting points are determined by capillary method and are uncorrected. Infrared spectra were recorded in KBr on I.R.—20 (Beckmann).

3-Arylisocoumarins : A mixture of homophthalic anhydride (1 mole), phenolic compound (1. 1 mole) and commercial-polyphosphoric acid (8 parts) was heated at 120-30° for one hour. The reaction mixture was worked up as reported in the previous communication[1] to afford 3-arylisocoumarins.

W-(2'-carboxyphenyl)-acetophenones : 3-Arylisocoumarin on treatment with aqueous sodium hydroxide (10%) and subsequent acidification furnished the keto acid. This could be cyclised back to original isocoumarin in the presence of acid.

3-Aryl-3, 4-dihydroisocoumarins : Reduction of the above keto acids in ethanolic sodiumhydroxide with sodiumborohydride yielded the corresponding dihydroisocoumarins.

Conversion of 3-aryl-3, 4-dihydroisocoumarins into 3-arylisocoumarins : A mixture of 3-aryl-3, 4-dihydroisocoumarin (1 mole), N-bromosuccinimide (1.1 mole) and benzoylperoxide (0.02-0.04g) in appropriate solvent (dry carbontetrachloride or dry benzene) on refluxing near an illuminated 60 watt lamp for about 4 hours gave 4-bromoderivatives which were not purified. Subsequent treatment of the 4-bromoderivatives with either triethyl amine or pyridine resulted in dehydrobromination providing respective 3-arylisocoumarins.

Acknowledgement

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*p*H Metric Study of Complexes of Some Metal Ions with Salicylaldehyde-4-*m*-Chlorophenyl-3-Thiosemicarbazone

Y. N. BHATT, K. K. PATEL, K. J. SHAH* & R. S. PATEL

Department of Chemistry, Saurashtra University, Bhavnagar.

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LIGANDS such as thiosemicarbazones are studied to a limited extent *p*H-metrically. Here salicylaldehyde-4-*m*-Cl phenyl-3-thiosemicarbazone *m*-Cl-SPT derivative is studied with metal like VO^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}. The formation constants for their metal were calculated by Calvin and Wilson *p*H titration technique as modified by Irving and Rossotti. The stability constants are determined in 50% aqueous dioxane medium.

* For correspondence.

Experimental

The ligand salicylaldehyde-4-*m*-chlorophenyl-3-thiosemicarbazone $C_6H_4Cl.NH.C(=S).N : CH.OH.C_6H_4$ was synthesized and crytallised to get analytically pure (m.p. 181°)[1]. The solution of *m*-Cl-SPT was prepared in dioxane (BDH, ANALAR grade) which was further purified by standard method of Vogel[2]. Metal nitrates used were of AnalaR grade which were estimated by standard gravimetric and volumetric methods. Philips *p*H meter was used for *p*H measurements. *p*H meter was calibrated with buffer solutions having *p*H 4.33 and 9.1 at 25°±1°.

All titrations were carried out in a 100 ml. beaker kept in water thermostat maintained at 25°±1°. Thirty five to forty five readings were taken in each case. Each titration was repeated to get reproducible results. The metal ligand ratio was maintained 1:5. The acid, reagent and metal titrations were carried out with 0.2 *M* NaOH and 50% v/v dioxane: water. The solution for blank titration contained 0.004 *M* HNO_3 and 0.1 *M* KNO_3. The solution for ligand titration contained 0.001 *M* ligand in addition to the blank solution. The solution for metal titration contained 0.0002 *M* metal ion [0.0001*M* for Co(II)] in addition to the ligand solution.

Results and Discussions

The practical proton-ligand stability constant for the ligand was calculated with the help of $\bar{n}_H$ values at different B values (*p*H meter readings in 50% aqueous dioxan-medium). $\bar{n}_H$ is calculated by the method of Irving & Rossotti[3] as adopted by Jabalpurwala et.al[4]. Plot of log $\bar{n}_H/1-\bar{n}_H$ against B is done to obtain a best straight line. From this straight line the values of the practical proton-ligand stability constant was obtained using the relation

$$\log P_{K_1}H = B + \log \frac{\bar{n}_H}{1-\bar{n}_H}$$

The proton ligand stability constant obtained is 9.55. For metal ligand stability constants $\bar{n}$ and pL were calculated by the method of Jabalpurwala et al[4]. The values of $\bar{n}$ are plotted against pL. The values of log K_1 were calculated by half integral method. The formation curve is given in Fig. 1. But for calculation of log K_2 least square method[5] in which $\frac{\bar{n}}{(1-\bar{n})HL}$ was plotted against $\frac{(\bar{n}-2)HL}{(1-\bar{n})}$ and Olerup's method was also used as there was not much difference between log K_1 and log K_2. The average stability constant are given Table-1.

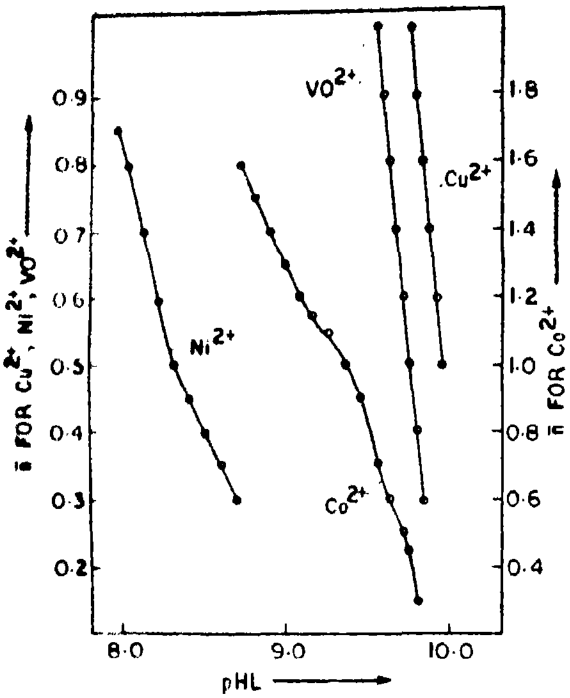


Fig. 1

TABLE 1

Metal	Log K_1	log K_2	logβ_2	σ
Cu^{2+}	9.96 ± 0.05	—	-	—
Co^{2+}	9.35 ± 0.05	9.38 ± 0.05	18.24 ± 0.05	0.063 ± 0.005
VO^{2+}	9.76 ± 0.05	-	—	—
Ni^{2+}	8.33 ± 0.05	-	—	—
H^+	9.55 ± 0.05	—	—	—

To check the validity of the results obtained by different methods for Co^{2+}, the $\bar{n}$ was recalculated taking log K_1 and log β_2 of least squares method as standard. There was not much difference between $\bar{n}$ calc. & $\bar{n}$ exptl. The value of σ standard deviation is 0.063.

For log K_1, it is observed that stability constants are in the order VO(II) ∠ Cu(II) > Co(II) > Ni(II).

Thus, Irving-Williams rule is obeyed except for the position of Co(II). This may be due to orbital stabilization of Co(II) complex.

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Book Review

INORGANIC CHEMISTRY – *By* **K. F. Purcell and J. C. Kotz, W. B. Saunders Co., Philadelphia (USA), 1977 ; xix + 1116 pp. ; price, US $ 25.50.** (Available through Macmillan Co. (India) Ltd.)

UNLIKE many of the texts in the subject commonly available in the market, which mostly enumerate the facts of chemistry without trying to help the students to enable them to understand the fascinating beauty of inorganic chemistry and its systematics, the authors of this treatise have used an innovative approach to unravel to the minds of the budding chemists the excitements and challenges of inorganic chemistry and promises for new developments in its different fields. The antiquated view held almost till recently that inorganic chemistry is primarily the chemistry of minerals and materials of inanimate origin has now been completely abandoned with a fuller knowledge and understanding of the vital role of several metal ions and some simple anions in biological systems, as well as with developments in the field of so-called organometallic chemistry. Another very significant development of the last two decades is the recognition of the importance of the understanding of inorganic reaction mechanisms in the elucidation and interpretation of many of the facts of inorganic chemistry. In fact, as the authors have stated in the 'Preface' a considerable amount of inorganic chemistry can be organized around mechanistic types and there should be greater emphasis on mechanisms in any modern treatment of the subject.

Of the nineteen chapters in this text the first four deal with fundamental concepts and their applications which really provide a strong foundation for the remaining text. This is followed by a chapter dealing with Lewis acid-base concept, solvent properties and solvation phenomena. The next two chapters (6 & 7) deal with structures and reactivities in terms of thermodynamic and mechanistic principles. In the next chapter (8) on the synthesis of important classes of non-metal compounds a very successful attempt has been made to reflect the importance of theories and basic principles in understanding the purposeful synthesis of molecules. The next three chapters (9-11) deal with coordination and transition metal chemistry and its various aspects such as bonding, structure, magnetic and spectral properties, isomerism, etc. The usefulness of a knowledge of mechanisms of electron transfer and ligand replacement reactions, molecular rearrangements and reactions of coordinated ligands in inorganic chemistry and its utility in the synthesis of a variety of inorganic compounds (complexes) is elegantly described in chapters 12-14. This is followed by three chapters (15-17) on the rapidly expanding field of organometallic chemistry, all of which have been dealt with due emphasis on reaction mechanisms. The last two chapters (18 & 19) deal with two other expanding areas of modern inorganic chemistry viz., chemistry of metal and non-metal cluster compounds and inorganic aspects of biochemistry ; this last one is indeed of great significance in the understanding of many of the vital life processes.

The text is a uniquely systematic, cohesive and exciting approach to inorganic chemistry which has greatly fulfilled the need for a modern text in the subject which will indeed be most useful to both the students and the teachers. It is also quite satisfying that on the prevailing American standard of pricing text books this voluminous treatise is fairly moderately priced. However, it is our hope that attempts would soon be made to bring out a cheaper edition to easily suit the means of its users in the developing nations.

D. Banerjea

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January to March 1977 Issue.

In page 1, read

linoleic ester as $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2CH\ CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2C{\scriptstyle\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR}}$

for $CH_3CH_2CH_2CH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C{\scriptstyle\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR}}$

oleic ester as $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2C{\scriptstyle\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR}}$

for $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2C{\scriptstyle\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OR}}$

In page 14, in scheme 3, the product on the left hand side which appears as :

$[MoN(PMe_2Ph)Cl_2(PMe_2Ph)_3]$

should read as :

$[Mo(NPMe_2Ph)Cl_2(PMe_2Ph)_3]$

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Ternary Complexes of Copper(II), Zinc(II), Nickel(II) and Cobalt(II) with Nitrilotriacetic Acid and Substituted Salicylic Acids

BIRENDRA K. AGRAWAL, KAMALAKAR DWIVEDI, MADHUP CHANDRA, BADRI V. AGARWALA and ARUN K. DEY*

Chemical Laboratories, University of Allahabad, Allahabad-211002

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Biligand complex forming systems of the type : M-NTA-L [M = Cu(II), Zn(II), Ni(II) and Co(II) ions ; NTA = nitrilotriacetic acid ; L = 5-nitrosalicylic acid (NSA) and 5-chlorosalicylic acid (CSA)] have been investigated potentiometrically [25°, μ=0.1*M* ($NaClO_4$), medium—50% *v/v* aqueous-ethanol]. Under identical conditions, the binary complexes of NSA and CSA have also been examined. The logarithms of the mixed ligand formation constants of complexes in M-NTA-NSA systems, $\log K^{M\,NTA}_{M.NTA.NSA}$ are 5.46, 4.28, 4.23 and 3.89 respectively. The logarithms of the first step formation constants of binary M-NSA complexes $\log K_1$ are 9.81, 7.22, 6.53 and 6.18 respectively. Only Cu(II) and Zn(II) complexes could be studied with CSA and the values of $\log K^{M.NTA}_{M.NTA.CSA}$ and $\log K_1$ are 5.46, 4.49 ; and 8.77, 7.26 respectively. The second step formation constants could be obtained only in the case of Cu-NSA and Cu-CSA systems, the values of $\log K_2$ being 7.11 and 6.46 respectively.

BINARY complexes of 5-nitrosalicylic acid[1-6] (NSA) and 5-chlorosalicylic acid[3] (CSA) with a number of metal ions have been reported in literature. The work described here deals with the investigation of ternary complexing systems of the type : M-NTA-L [M=Cu(II), Zn(II), Ni(II) and Co(II) ; NTA=nitrilotriacetic acid and L=NSA and CSA] involving NTA as a primary and L as secondary ligands at 25° and at an ionic strength of 0.1 *M* ($NaClO_4$) in 50% *v/v* aqueous-ethanol medium adopting Irving and Rossotti *p*H-titration technique[7] as modified by Chidambaram and Bhattacharya[8]. Studies on the binary complexes of the secondary ligands under identical conditions have also been examined. Though such studies with NSA in aqueous medium have already been reported [1,6], no work appears to be on record on CSA with the ions studied here.

Experimental

Solutions and related materials :

Solutions of copper (II), zinc (II), nickel (II) and cobalt (II) perchlorates were prepared and standardized[9]. Suitable volumes of these solutions were separately diluted and perchloric acid added if necessary to obtain 0.01 *M* metal perchlorate in 0.02 *M* perchloric acid. A stock solution of sodium perchlorate (1.0 *M*) was prepared and standardized[10].

Stock solutions of CO_2-free sodium hydroxide (0.098 *M*) and perchloric acid (0.02 *M*) were prepared and used after standardization. Solutions of the chelating agents (0.005*M*) viz. nitrilotriacetic acid (in water) ; 5-nitrosalicyclic acid (in ethanol) and 5-chlorosalicylic acid (in ethanol) were prepared by direct weighing.

All the reagents used were of analytical grade.

Procedure :

Measurements were carried out using Leeds and Northrup *p*H-meter with a glass-calomel electrode assembly at 25°. The medium was 50% *v/v* aqueous ethanol and ionic strength 0.1 *M* ($NaClO_4$).

(*a*) *M-L Systems :*

Three titration mixtures (total volume 50.0 ml), viz. (A) acid, (B) ligand, and (C) chelate were prepared[11]. The concentrations were : N°=0.098 *M* ; E°=0.002 *M* ; $TC_T°$=0.001 *M* ; and TC_M=0.0002 *M* (symbols having usual meanings[7]). Mixtures A, B and C were individually titrated against standard alkali and thus three titration curves A, B and C were obtained for each system. For illustration titration curves of only M-CSA systems (fig. 1) are being given here.

(*b*) *M-NTA-L systems :*

Mixtures containing (D) 5.0 ml perchloric acid (0.02 *M*)+5.0 ml sodium perchlorate (1.0 *M*)+10.0 ml NTA (0.005 *M*)+5.0 ml water+25.0 ml ethanol ; (E) 5.0 ml metal perchlorate (0.01 *M* in 0.02 *M* perchloric acid)+5.0 ml sodium perchlorate (1.0 *M*) +10.0 ml NTA (0.005 *M*)+5.0 ml water+25.0 ml

*To whom correspondence should be addressed.

ethanol ; (F) 5.0 ml perchloric acid (0.02 *M*)+7.5 ml perchloric acid (0.02 *M*) (to account for the protons liberated as a result of complexations of NTA with all the M-L systems investigated, precipitation occurred even before the stage of 1 : 1 or 1 : 2 [only in case of Cu(II)] complexation was complete, and no

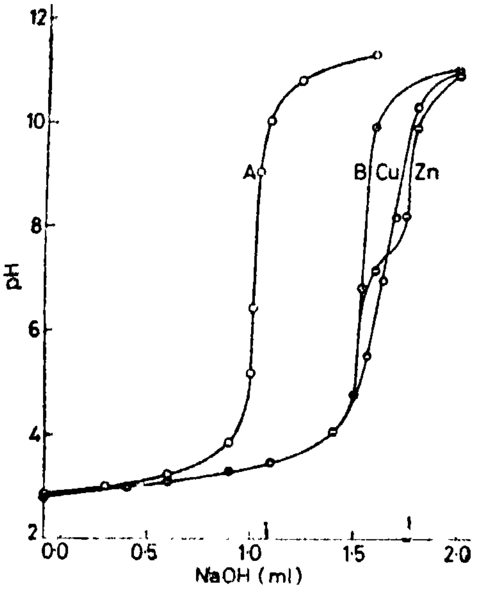


Fig. 1 Titration curves M-CSA systems -O-O—acid (A) ; -×-×-CSA (B) ; -O-O-Cu(II)-CSA-.⊖-⊖-Zn(II)-CSA

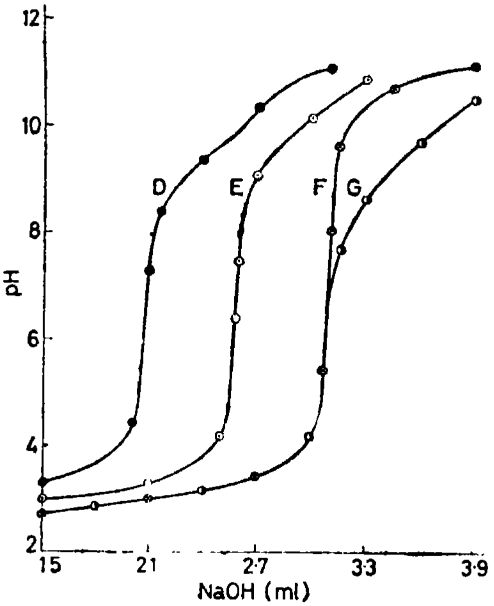


Fig. 2 Titration curves Cu(II)-NTA-NSA system -●-●-NTA (D) ; -O-O-Cu(II)-NTA (E) ; -×-×-NSA (F) ; -◐-◐-Cu(II)-NTA-NSA (G)

metal ions)+5.0 ml sodium perchlorate (1.0 *M*)+ 10·0 ml NSA or CSA (0·005 *M*)+7·5 ml water+ 15·0 ml ethanol and (G) 5·0 ml metal perchlorate (0·01 *M* in 0·02 *M* perchloric acid)+5·0 ml sodium pechlorate (1·0 *M*)+10·0 ml NTA (0·005 *M*)+ 10·0 ml NSA or CSA (0·005 *M*)+5·0 ml water+ 15·0 ml ethanol were prepared. The excess acidity in mixtures F and G as compared to A was taken into account in the calculations. The mixtures were separately titrated against standard alkali, whereby titration curves D, E, F and G in each of the systems were obtained. Titration curves of only Cu(II)-NTA-NSA system are being given here (Fig. 2).

Calculations

M-L Systems :

From the titration curves A, B. and C (curve C designated by the respective metal ions in fig. 1), the parameters $\bar{n}_A$, average number of protons associated with the ligand L, $\bar{n}$, average number of ligand molecules attached per metal ion and *p*L, free ligand exponent were calculated using the formulae of Irving and Rossotti[7], and the formation constants corresponding to the proton-ligand metal-ligand systems obtained by average value method are recorded in Table 1.

The absence of polynuclear species etc. was confirmed by using several concentrations of the reactants and the results obtained were identical. In studies beyond this stage were possible. Hence, the hydroxospecies likely to be formed after this stage could not be studied.

TABLE—1 STABILITY CONSTANTS OF BINARY (M-L) AND TERNARY (M—NTA–L) CHELATES IN 50% v/v AQUEOUS-ETHANOL MEDIUM (25°, μ = 0.1)

Cation	log K_1	log K_2	$\log K^{M.NTA}_{M.NTA.L}$
	(a) *Secondary ligand : NSA*		
H^+	11.01	2.86	—
Cu(II)	9.81	7.11	5.46
Zn(II)	7.22	—	4.28
Ni(II)	6.53	—	4.23
Co(II)	6.18	—	3.89
	(b) *Secondary ligand - CSA*		
H^+	11.52	3.19	—
Cu(II)	8.77	6.49	5.46
Zn(II)	7.26	—	4.49

M-NTA-L systems :

Complete formation of (M. NTA)$^-$ complex species occurs at *p*H≈4, which remain stable at higher *p*H values [analyses of curves A (fig. 1), D and E (fig. 2)]. The mixed ligand titration curve G departs from the secondary ligand titration curve F, after complete formation of (M.NTA)$^-$ species in all the systems. It may thus be assumed that the secondary ligand NSA or CSA would combine with (M. NTA)$^-$ species in ternary systems similarly as it does with $[M.(H_2O)_n]^{2+}$ in the binary systems.

The horizontal distance between the curves G and F were used for the calculation of $\bar{n}_{mix}$, the average number of NSA or CSA molecules attached per $(M.NTA)^-$ ions using the equation :

$$\bar{n}_{mix} = \frac{(v^G - v^F)(N^o + E^o)}{(V^o + V')\bar{n}_A TC_{M.NTA^o}} \quad \ldots \quad (1)$$

where v^G and v^F are the volumes of alkali consumed to reach the same *p*H-values in the curves G and F of the mixed ligand systems. $TC_{M.NTA^o}$ is the concentration of $(M.NTA)^-$ complex which is, equivalent to the initial metal ion concentration. All other symbols have their usual meanings[7]. $\bar{n}_A$ values at different *p*H were available from the binary complexing systems. From the values of $\bar{n}_{mix}$ so obtained, free ligand exponent, pL_{mix} were calculated using the equation :

$$pL_{mix} = \log_{10} \left[\frac{\sum_{n=0}^{j} \beta^H_n \left(\frac{1}{\text{anti log B}}\right)^n}{(TC_{L^o} - \bar{n}_{mix}.\ TC_{M.NTA_o})} \cdot \frac{V^o + V}{V^o} \right] \quad \ldots \quad (2)$$

Formation curves corresponding to various mixed ligand systems were obtained by plotting $\bar{n}_{mix}$ *vs* pL_{mix} (figs. omitted) and the corresponding formation constants obtained by average value method are recorded in table 1.

Results and Discussion

Proton-ligand systems :

The formation curves of the ligands NSA or CSA (figs. not showm) exhibit a wave like shape suggesting two distinct steps corresponding to the protonation of carboxylate group and the phenolic oxygen of the ligands.

It is well known that the presence of electron withdrawing nitrogroup in phenols or benzoic acid increases their acidity. Similarly chloro group, in general, exerts an electron withdrawing inductive effect, but also an electron donating mesomeric effect, when located at *ortho*- or *para* positions to either of them. Further the inductive effect is more pronounced with nitro group than the chloro group[13]. The influence of the location of nitro group in NSA and chloro group in CSA thus results in the protonation constants of NSA being less than those of CSA (Table 1).

Binary systems :

In the M-L binary systems Cu(II) forms both 1:1 and 1:2 complexes, while other ions form only 1:1 (1:2 complex species could not be examined as explained). The formation of complexes, in systems Ni(II)-CSA and Co(II)-CSA, however, seemed to be doubtful as the $\bar{n}$ values were appreciably low to provide any reliable value of stability constants, and hence these systems have not been pursued.

The stabilities of the metal complexes (Table 1) follow the trend :

$$Co(II) < Ni(II) < Cu(II) > Zn(II)$$

which is in conformity with the Irving-Williams order[18]. Also, values of log K_1 (K_1 = first step formation constant in M-L systems) for various complexes other than that of copper (II) are fairly close to each other. The stabilities of copper (II) complexes are usually higher than could be expected from ionic radius or electro-negativity considerations[14]. This additional stability of copper(II) complexes may be attributed to the unique electronic configuration (d^9) of Cu(II) ion which is capable of additional stabilization due to Jahn-Teller distortion.

The Irving-Williams order runs roughly parallel to the second ionization potential of the elements which provides information on the affinity of the central atom to accept electrons from the ligands in covalent bond formation. The log K_1 values for the metal complexes were thus plotted against the respective second ionization potentials and a straight line was obtained (fig. 3). The point corresponding to Ni(II), however, does not fall on the line and is below it, showing that nickel(II) complexes possessed a low degree of stability with the ligand (NSA).

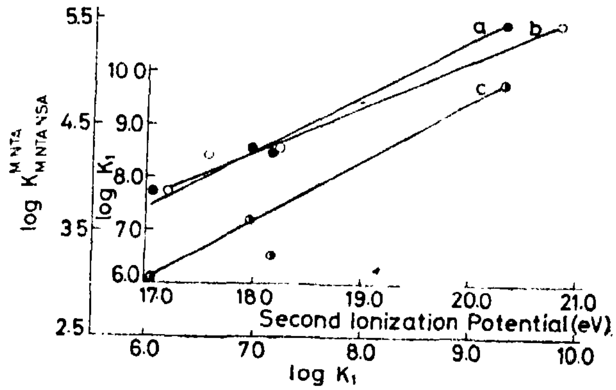


Fig. 3 log $K^{M.NTA}_{M.NTA.NSA}$ *vs* second ionization potential(a); log $K^{M.NTA}_{M.NTA.NSA}$ *vs* log K_1 (b) ; log K_1 *vs* second ionization potential(c).

Ternary Systems :

It is observed that the values of log $K^{M.NTA}_{M.NTA.L}$

($K^{M.NTA}_{M.NTA.L}$ = stoichiometric mixed ligand complex

formation constant in M-NTA-L systems) is less than log K_1 and even less than log K_2 (K_1 and K_2 are the step formation constants of the binary complexes of the secondary ligands). This behaviour can be explained on the basis of coulombic interactions between various ligand anion species present. In the mixed ligand complex formation there is repulsion between two negative charges from the secondary ligand anion and three negative charges from the NTA anions. The extent of this repulsion would obviously be more than that encountered between two negative charges each from the two secondary ligand anions, in the formation of ML_2 species, ultimately resulting in $\log K^{M.NTA}_{M.NTA.L} < \log K_2$. No such interaction is encountered in the formation of ML species. The value of log K_1 being greater than log K_2 are well established, which then finally justifies the order $\log K_1 > \log K_2 > \log K^{M.NTA}_{M.NTA.L}$

In all the ternary systems studied, the order of stability of mixed ligand complexes with respect to the metal ions was found to be

$$Co(II) < Ni(II) < Cu(II) > Zn(II)$$

which is the same as in corresponding binary M-L systems.

The plot of $\log K^{M.NTA}_{M.NTA.L}$ *vs* log K_1 (fig. 3) gives a straight line indicating that the process of association of L with $(M.NTA)^-$ species in the ternary systems follows, in general, the same pattern as that during the association of L with $[M(H_2O)_n]^{2+}$ in the corresponding binary complexing systems.

Acknowledgement

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Polarographic Studies on the Complexes of Zn, Cd and Pb with Thiovanol

K. M. KANTH

P. G. Deptt. of Chemistry, Bhagalpur University, Bhagalpur-812007

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The complex formation of Zn(II), Cd(II) and Pb(II) with thiovanol has been studied polarographically in acetate buffer which shows a stoichiometry of 1: 2: : Metal: Ligand. Zn(II) gives an irreversible, Cd(II) a quasireversible and Pb(II) a reversible reduction wave in acetate buffer. The forward rate constant K_f^0 in case of Zn and Cd have been found to be 7.768×10^{-16} moles $litre^{-1}$ sec^{-1} and 3.477×10^{-14} moles $litre^{-1}$ sec^{-1} respectively. The dissociation constant for the Pb-TV complex ion being 3.9×10^{-8}. The transfer coefficient (α) for Cd-TV complex is 0.681.

THE present interest on compounds containing sulphydryl group is due to their usefulness in medicine[1], biology[2], industry[3], and analytical chemistry[10]. In continuation of our work on complexes of thiovanol with transition metals[11, 12] the present paper describes the polarographic studies on the complexes of thiovanol ($CH_2SHCHOHCH_2OH$) with Zn, Cd and Pb in aqueous medium. The results of studies show that metal : ligand ratios in the complexes are 1 : 2. The forward rate constants, for Zn-TV and Cd-TV complexes, transfer coefficient for Cd-TV complex and the dissociation constant for Pb-TV complex have been calculated. (TV=Thiovanol).

Materials and Methods

Stock solutions of lead nitrate and cadmium sulphate were prepared in double distilled water from BDH analaR grade and that of Zinc was prepared by dissolving Zinc Oxide BDH analaR in minimum quantity of dilute HCl. All experiments were done in aqueous medium. All the measurements were made at 26°±0.1° in air-free media and under nitrogen atmosphere.

Polarographic measurements were made using a mannual circuit as recommended by Kolthoff and Lingane[4]. Measurements were made with Hume and Harris[5] saturated Calomel electrode as reference electrode. The characteristics of the d.m.e. capillary used were as follows :

$m=2.012$ mg/sec $\quad$ $t=3.70$ seconds
$m^{2/3}t^{1/6}=2.003$ $mg^{2/3}sec^{-1/2}$

height of the mercury column h=36.4 cm. Studies were made in acetate buffer. A Leeds Northrup *p*H meter, with a general purpose glass electrode was used for the *p*H measurements. All the other Chemicals used were of analaR grade.

Results and Discussions

Polarographic measurements on the complexes were made in aqueous medium and acetate buffer (*p*H 4.8) and at a constant ionic strength $\mu=0.2M$ in the presence of KNO_3 as supporting electrolyte.

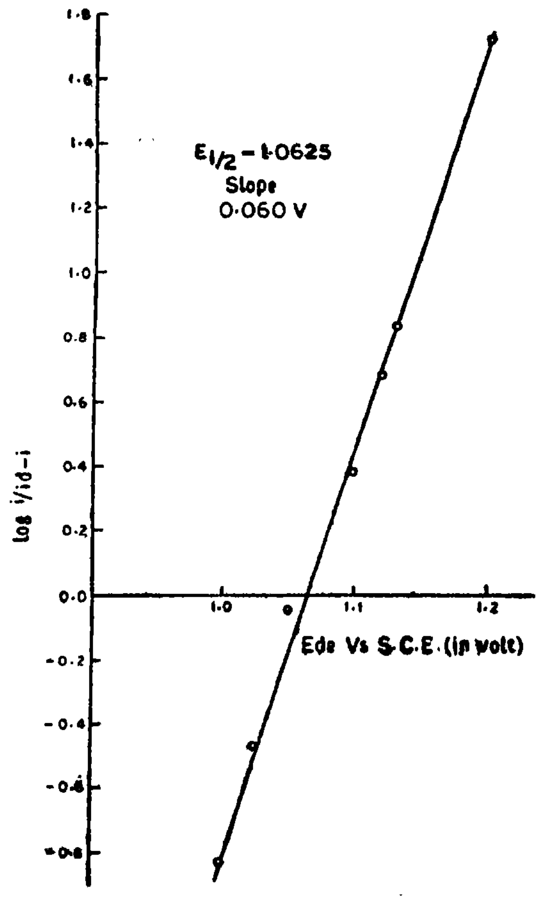


Fig. 1. System Zinc -TV

Half-wave potential ($E_{\frac{1}{2}}$) values for Zn-TV (−1.05 volt Vs SCE), Pb-TV(− 0.425 volt Vs SCE) and Cd-TV (−0.63 volt Vs SCE) were observed to shift towards more negative potentials. The values obtained for the $E_{\frac{1}{2}}$ of the complexed metal ions in different concentrations of the ligand are given in Table 1.

TABLE – 1 CHARACTERISTICS OF THE WAVES OF ZINC, CADMIUM AND LEAD IONS IN THE PRESENCE OF TV(METAL ION CONCENTRATION $1.0\times10^{-8}M$)

Zinc-TV		Cadmium-TV		Lead-TV	
[TV] $M\times10^{-8}$	$E_{\frac{1}{2}}$(V)	[TV] $M\times10^{-8}$	$E_{\frac{1}{2}}$(V)	[TV] $M\times10^{-8}$	$E_{\frac{1}{2}}$(V)
2.16	−1.0625	2.16	−0.6425	2.16	−0.4315
4.32	−1.0715	4.32	−0.6450	4.32	−0.4400
6.48	−1.0750	6.48	−0.6500	6.48	−0.4450
8.64	−1.0770	8.64	−0.6580	8 64	−0.4475
10.80	−1.0770	10.80	−0 6580	10.80	−0.4475

Zn-TV complex : Zn (II) gave a two electron irreversible reduction wave. The polt of log *i/id-i* Vs E_{de} gave a straight line with slope 0.060 volt (Fig 1). This proves the irreversibility of the system. The polt of $E_{\frac{1}{2}}$ Vs log C of thiovanol was a stright line with a slope of 0.071 volt (Fig 2). The following electrode reaction may be proposed.

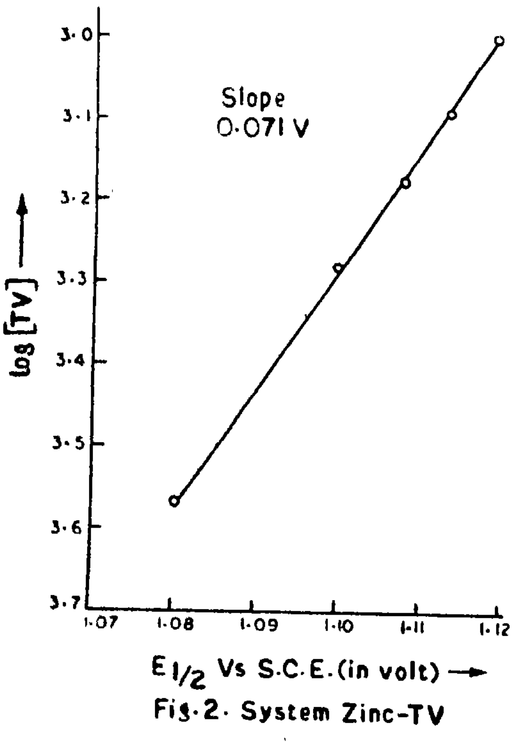


Fig. 2. System Zinc-TV

$Zn(TV)_2^{2+} + 2e \xrightarrow{+Hg} Zn(Hg) + 2TV$ (charge contribution of TV has been ignored).

The kinetic parametres of the irreversible and quasireversible wave can be studied by Matsuda and Ayabe equation[6,7].

$$(E_{\frac{1}{2}})C = \frac{0.06}{\alpha n}\left[\log\frac{K^{\circ}_{f}}{\sqrt{D_N}}f_N + \tfrac{1}{2}\log T - 0.053 - \log\left(\frac{i_l}{i_d}\right) - (N-P)\operatorname{Log} f_x C_x\right] \quad ......(1)$$

where $(E_{\frac{1}{2}})C$ = Half-wave potential Vs NHE, K°_{f} = forward rate constant at potential of NHE, D_N = diffusion coefficient of complex ion in solution, T = droptime at $E_{\frac{1}{2}}$, i_d = diffusion current, i_l = limiting current, f_N = activity coefficient of complex ion, f_x = activity coefficient of ligand, C_x = concentration of ligand

and f_N and $f_x = 1$ $\left(\frac{i_l}{i_d}\right) = 1$. The value of K°_{f} for ZnTV system has been found to be 7.768×10^{-10} litre^{-1} sec^{-1}.

Pb-TV complex : Pb(II) gave a two electron, reversible reduction wave. A plot of log (i/id-i) Vs E_{de} gave a straight line with a slope of 0.030V (Fig 3). The plot of $E_{\frac{1}{2}}$ Vs log C of TV gave a slope of 0.056 V (Fig 4).

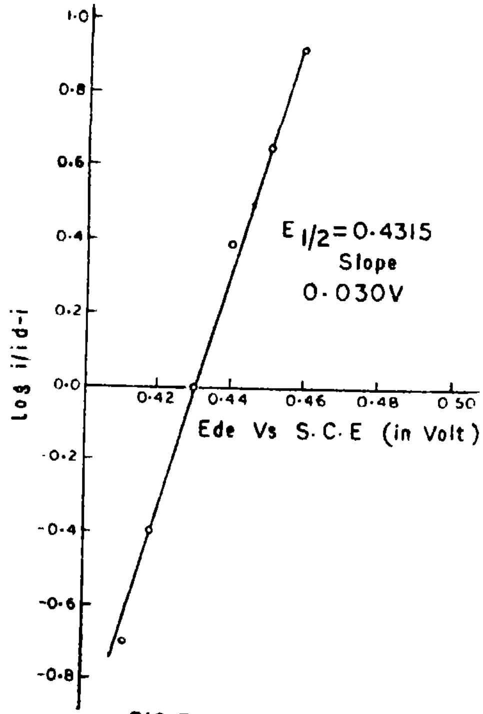


FIG.3 System Lead-TV

Applying the equation[8]

$$\frac{dE_{\frac{1}{2}}}{d\log[TV]} = \frac{0.060}{n}(p-q) \quad ....(2)$$

where n is the number of electrons involved in the reduction, p and q are number of ligand groups attached to the oxidised and reduced forms respectively. The value of p was found to be very nearly two when q=0 and n=2 in equation (2). The value of

dissociation constant was calcuated using Lingane[8] equation and came out to be 3.9×10^{-8}. The electrode reaction may be represented as $Pb(TV)_2^{2+}$+ $2e^- \rightleftharpoons Pb(Hg) + 2TV$ (Charge contribution of TV
+Hg
has been ignored).

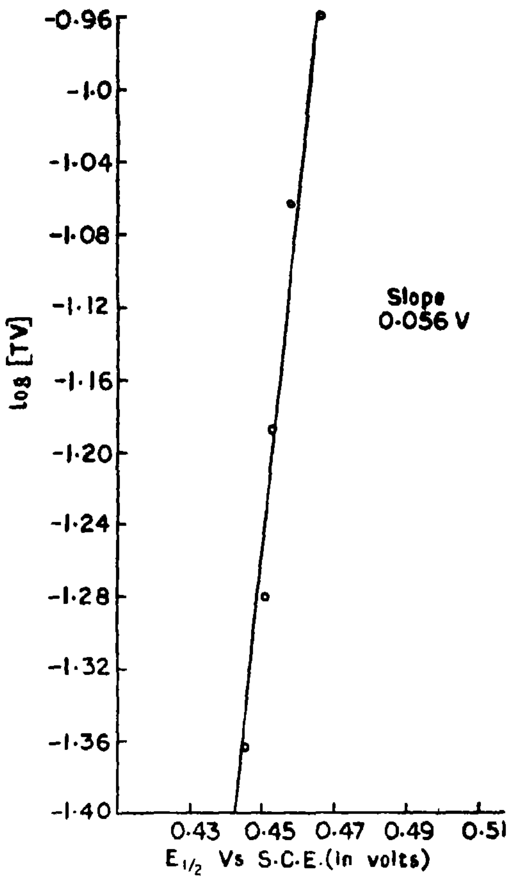


FIG.4. System Lead-TV

Cd-TY complex: Cd(II) gave a two electron quasi-reversible reduction wave. The plot of log(i/id-i) gave a straight line with a slop of 0.044 V which is higher than the value expected for two electron reversible reduction (0.0296 V at 30° (Fig.5). The plot of $E_{\frac{1}{2}}$ Vs logC of TV was a straight line with a slope of 0.045V (Fig 6). Thus the electrode is not reversible and may be treated as quasireversible. The value of transfer coefficient (α) came out to be 0.681. The forward rate constant (K°_f) was found to be 3.477×10^{-19} moles $liter^{-1}$ sec^{-1} using Matsuda and Ayabe equation[6,7]. The electrode reaction may thus be proposed as

$$Cd(TV)_2^{2+} + 2e^- \rightleftharpoons Cd(Hg) + 2TV$$
+Hg

(Where charge contribution of TV has been ignored).

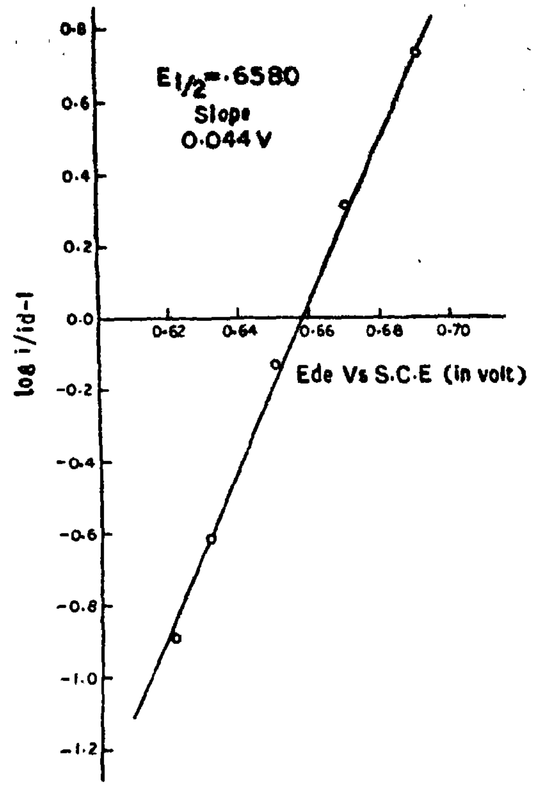


Fig.5. System cadmium TV

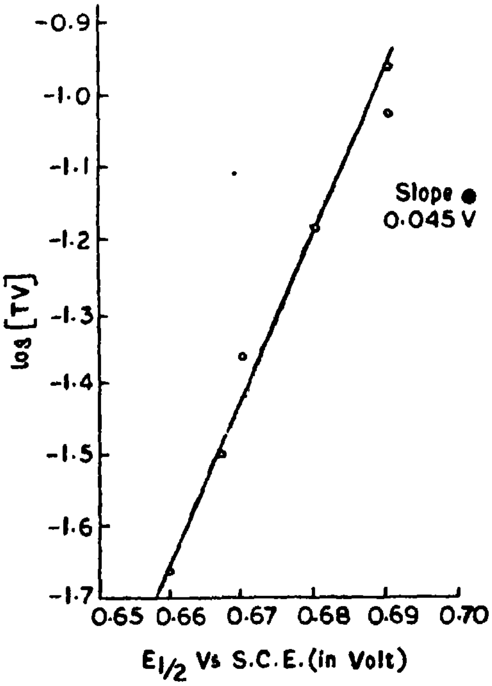


Fig.6. System cadmium TV

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Polarographic Reduction of two Azo Dyes : DPP and SPADNS

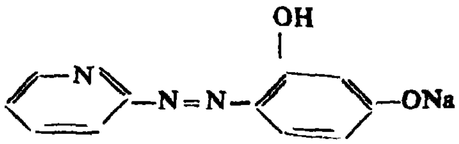
WAHID U. MALIK[a], RAMESH BEMBI[b], R. N. GOYAL, OM PRAKASH TANDON and R. K. PALIWAL[c]

Department of Chemistry, University of Roorkee, Roorkee

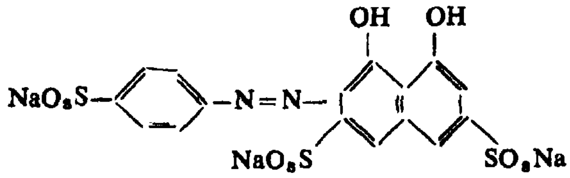
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DPP and SPADNS, two well known azodyes give one well defined, 2-electron transfer, diffusion controlled, reversible cathodic wave up to pH 5.5, after which one more wave appears at lesser negative potential. This wave is due to the possible role of adsorption. After pH 5.5, the main wave also shows irreversible behaviour.

Azo dyes constitute an important class of mordant dyes used for dyeing of fibres[1]. From the analytical view point also they are invaluable for trace analysis[2] of rare metals like zirconium, cerium, thorium etc. Although wide ranging studies have been carried out on the metal complexes of these dyes, little attention has been paid to their polarographic reduction. Two azo dyes DPP and SPADNS, having the structures given below, have therefore been studied polarographically.



DPP
4-(2-Pyridylazo) resorcinol



SPADNS
4,5-Dihydroxy-3-(p-sulpho phenylazo)-2,7-naphthalenedisulphonate.

Fig. 1.

Experimental

DPP and SPADNS were E. MERCK and LOBA CHEMIE AUSTRANAL products respectively. They were purified by crystallisation from 50% ethanol. After drying over silica gel, they were checked for their purity by paper chromatography.

Stock solutions (1×10^{-3}M) of the dyes were prepared in doubly distilled water. They were studied polarographically in Walpole-Acetate buffer[3], (*p*H 2.0-5.5) and Britton Robinson buffers[4] (*p*H 5.5-12.0). The *p*H of the buffers was checked with an Elico-LI-10 *p*H meter, using glass electrodes.

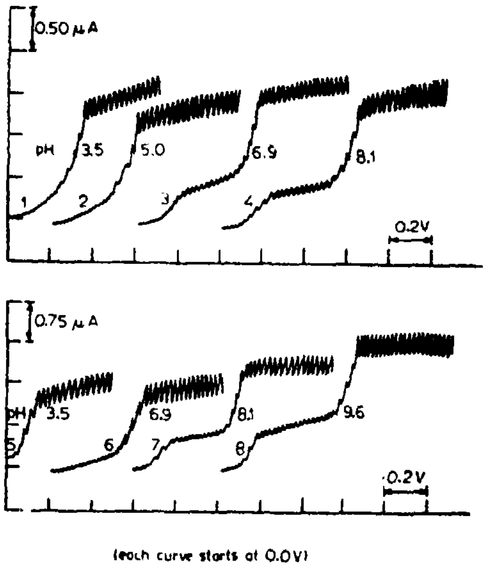


Fig.2. Typical polarograms of dyes SPADNS (1-4) and DPP (5-8) at various pH ($C=1.0\times10^{-4}$M)

Polarographic curves were recorded at 30± 0.1° on a Cambridge pen recording polarograph using a Fischer Capillary having a capillary characteristic of $(m^{2/3} t^{1/6})=1.5276$ $mg^{2/3}$ $s^{-1/2}$. A saturated calomel electrode was used as reference electrode and 0.1 *M* KCl as supporting electrolyte. In the case of DPP, no maxima suppressor was used, while a freshly prepared gelatin solution (0.005%) was used in the case of SPADNS over the entire *p*H range studied.

In the case of DPP, 8.0 ml of buffer +1.0 ml of

(a) Present address : Bundelkhand University, Jhansi (U.P.).
(b) To whom all correspondence may be addressed.
(c) Department of Chemistry, Gurukul Kangri University, Hardwar.

1·0*M* KCl+1.0 ml of the dye and with SPADNS 7.5 ml of buffer+1.0 ml KCl+1.0 ml dye+0.5 ml gelatin were thoroughly mixed and deaerated by passing a stream of hydrogen gas for about 15 minutes. The number of electrons involved in the reduction were determined by log plots as well as by the millicoulometric method of DeVries and Kroon[4]. The temperature coefficient for the reduction of these dyes was determined by Nejedlys method[5].

Results and Discussions

Typical polarograms for DPP and SPADNS are given in fig. 2. and the polarographic characteristics are given in Table 1. Both DPP and SPADNS give

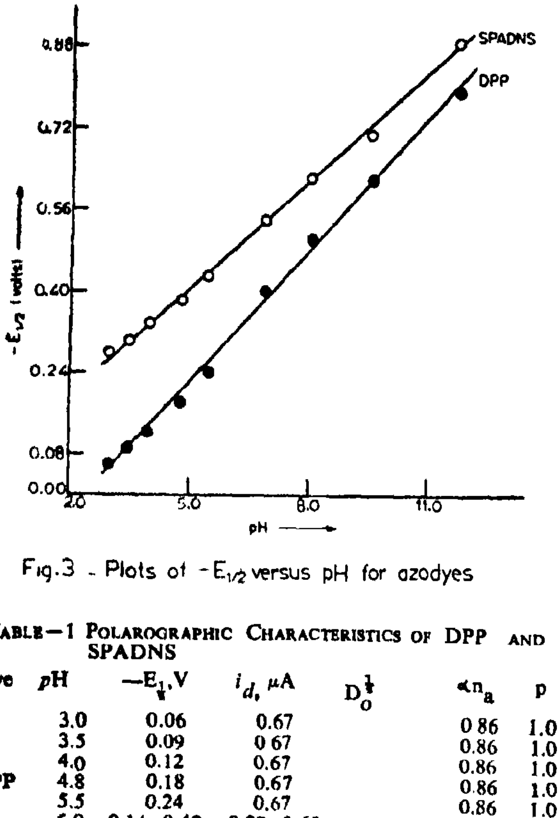


Fig.3 - Plots of $-E_{1/2}$ versus pH for azodyes

TABLE—1 POLAROGRAPHIC CHARACTERISTICS OF DPP AND SPADNS

Dye	*p*H	$-E_{\frac{1}{2}}$,V	i_d, μA	$D_o^{\frac{1}{2}}$	αn_a	p
	3.0	0.06	0.67		0 86	1.0
	3.5	0.09	0 67		0.86	1.0
	4.0	0.12	0.67		0.86	1.0
DPP	4.8	0.18	0.67		0 86	1.0
	5.5	0.24	0.67		0.86	1.0
	6.9	0.14, 0.40	0.27, 0.65		0.86	1.0
	8.1	0.14, 0.48	0.27, 0.704	.04 × 10^{-6}	0.94	1.1
	9.6	0.14, 0.62	0.27, 0.75		0.94	1.1
	3.0	0.28	0.85		0.79	0.9
	3.5	0.30	0.85		0.86	1.0
SPADNS	4.0	0.34	0.85		0 79	0.9
	4.8	0.37	0.85		0 86	1.0
	5.5	0.43	0 85		0.86	1.0
	6.9	0.54	0.87		0.86	1.0
	8.1	0.18, 0.62	0.40, 0.85	4.58 × 10^{-6}	0.86	1.0
	9.6	0.18, 0.70	0.40, 0.90		0.86	1.0
	11.8	0.18, 0.88	0.40, 0.90		0.86	1.0

a single two electron transfer reduction wave up to a *p*H of 8.1. However at *p*H values greater than 8.1 another wave appears at lesser negative potentials than the main wave. The main wave was found to be diffusion controlled as evinced by the linear plots of i_d versus $\sqrt{h}$ and i_d versus concentration. The diffusion controlled nature was further evident from the values of the temperature coefficient which are below 1.6%K^{-1}. The wave height was also found to be independent of *p*H.

Log plots showed the reversible nature of the waves up to a *p*H of 5.5, while beyond this *p*H the waves were found to be irreversible. A similar behaviour has also been reported in the case of azobenzene[6] and some other azo dyes[7,8].

The dependence of $E_{\frac{1}{2}}$ on concentration was studied at *p*H 8.1. For both the dyes, the $E_{\frac{1}{2}}$ was found to be independent of concentration in the range 0.5-3.0×10^{-4}*M*. It was further observed that the height of the pre-wave was independent of concentration and hence this wave may be assigned to the adsorption of the dye at the d.m.e. (adsorption wave).

The $E_{\frac{1}{2}}$ of the main wave (post wave) showed shift towards negative potentials with increase in *p*H while the diffusion current remained constant in the entire *p*H range. The plots of $E_{\frac{1}{2}}$ versus *p*H were linear (Fig. 3) having a slope of 60 mv/*p*H in the case of SPANDS and 75 mv/*p*H for DPP.

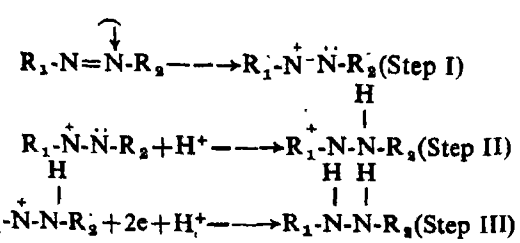
The values of αn_a (product of transfer coefficient and number of electrons involved per molecule of reactant in the rate determining step of the electrode process) and p (the number of H^+ ions involved per molecule of reactant in the rate determining step) were calculated (Table 1) using the following expressions :

$$E_{\frac{3}{4}} - E_{\frac{1}{4}} = -\frac{0.0517}{\alpha n_a}$$

$$\frac{d\,(E_{\frac{1}{2}})}{d\,(pH)} = -\frac{0.05915\,p}{\alpha na}$$

The number of electrons involved in the reduction of the dye, as determined by the millicoloumetric method, were found to be 2.

Keeping in view a two electron reduction process, the following scheme can be proposed for these dyes :



The values of p is in accord with the rate determining step (II) where only one H^+ ion is involved.

The polarisation step (I) and step (III) are both known to be very rapid.

A similar mechanism has also been proposed by Zuman[10] and others[8,11,12] for other azo compounds.

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Some Aspects of Copper by Calcium Hydroxylapatite

PREMA N. PATEL AND S. V. CHIRANJEEVI RAO*

Post-Graduate Department of Chemistry, G. M. College, Sambalpur

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$Ca^{2+} \rightarrow Cu^{2+}$ exchange in synthetic hydroxylapatite is facilitated by an increase in Cu^{2+} concentration, a decrease in pH of the medium of exchange and in the particle size of hydroxylapatite. Adsorption of Cu^{2+} and its accompanying diffusion into the interion of the crystals of hydroxylapatite explain the mechanism of exchange.

CALCIUM hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$, (CaHA) is the principle inorganic component of human skeletal system[1], has been the subject of extensive biological and physico-chemical studies due to its ability to undergo both cationic and anionic exchanges. The $Ca^{2+} \rightarrow Cu^{2+}$ replacement is of extreme biological significance as it explains the mechanism of incorporation of copper into human skeletal system according to the following equation $Ca_{10}(PO_4)_6(OH)_2 + n\,Cu^{2+} \rightarrow Ca_{(10-n)}Cu_n(PO_4)_6(OH)_2 + nCa^{2+}$.

Experimental

The synthetic CaHA was prepared by modified Collin's method[2] and heated to constant weight at 110°. The molar Ca/P value was found by complexometric method[3] to be 1.68 (theoretical value 1.67). The period of equilibration required for the attainment of saturation of the exchange was determined through kinetic studies. The dependence of uptake of copper by CaHA on factors like *p*H of the medium of equilibration in the physiologically important range of 5.0 to 8.0, concentration of Cu^{2+} ion in the range between 0.01 *M* to 0.1*M* of $Cu(NO_3)_2$ and a particle size between 45 μ to 250μ and the kinetics of $Ca^{2+} \rightarrow Cu^{2+}$ exchange were investigated. 0.2 g of CaHA was equilibrated with a solution of 100 ml of $Cu(NO_3)_2$ A.R. (BDH) by shaking in air tight polyethylene containers mechanically changing the factors effecting the uptake under investigation each time while other factors were kept constant. The experimental assembly was kept in thermally insulated cabin to maintain at 37 ± 0.5° to simulate biological conditions. At the end of desired period of equilibration the contents were filtered through IG_4 crucible. The residue was washed with doubly distilled water till it is free from adsorbed copper and the calcium and copper content of the residue was determined by method specially worked out for this purpose[4].

Results and Discussion

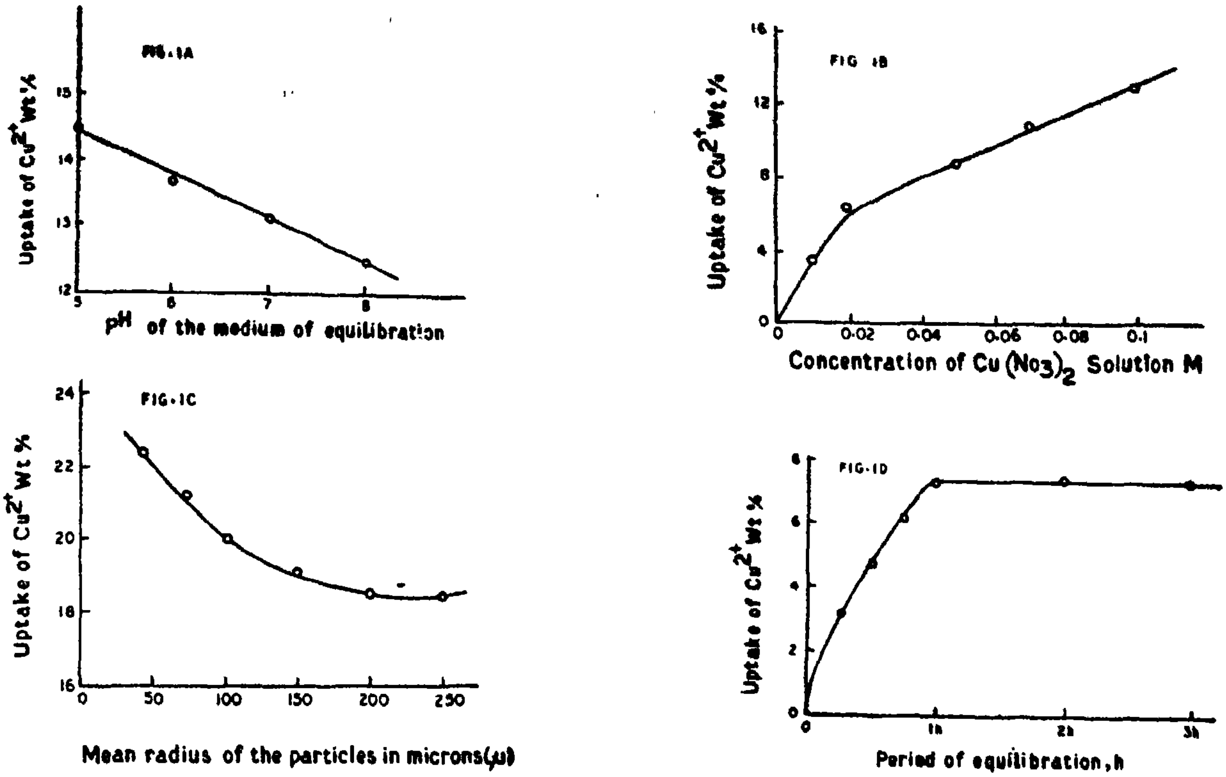
The results of uptake of copper by CaHA were represented diagramatically Fig. 1. The uptake of Cu^{2+} by CaHA was found to (i) decrease with increase of *p*H of the medium of equilibration in the physiologically important range of 5.0 to 8.0 (ii) increase with increase of concentration of Cu^{2+} ion and (iii) increase with decrease in the particle size of CaHA. The uptake of Cu^{2+} is found to be very rapid initially within the first 60 min (7.4 wt %) and remains almost constant (Fig. 1). The uptake varies linearly from 12.5 to 14.5 wt % as the *p*H decreases from 8.0 to 5.0 (Fig. 1A), it was also a linear function of increase from 3.4 to 13.1 wt % as the concentration of the medium of $Cu(NO_3)_2$ solution increases from 0.01 to 0.1*M* (Fig. 1B). Fig. 1C shows that the uptake under a given set of experimental conditions increases from 18.6 to 22.4 wt % as the mean radius. of the particles decreases from 250 μ to 45 μ.

The fact that the exchange increases with a decrease in the particle size of CaHA (Fig. 1C) and with an increase in Cu^{2+} concentration)Fig. 1 B) leads to the conclusion that the first rapid stage is surface dependent and the second stage of the exchange may be diffusion controlled and hence slow.

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* For correspondance, Present address :
Chemist, Hindustan Zinc Ltd., Visakhapatnam-15.



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Bromoarsenate(III) Complexes-I

N. K. JHA and S. S. A. RIZVI
Department of Chemistry, Indian Institute of Technology, New Delhi-110029
and
BIVEKANAND MISHRA*
Department of Chemistry, Sahibganj College, Sahibganj (S. P.), Bihar

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New method of preparation of double salts containg tetrabromoarsenate and amine hydrobromide of the type A_2AsBr_5 (A = Substituted ammonium cation) rebresented as A $AsBr_4$: A Br and A_3AsBr_6 as A $AsBr_4$: 2ABr in aqueous hydrobromic acid medium with their properties and characterisation has been reported.

POPOV[1] had investigated the reactions of arsenic tribromide with salts of organic bases in chloroform medium. He reported that four main types of double bromides differing in the ratio of $AsBr_3$: Salt of organic base were formed ; the ratios found were 1 : 1, 1 : 2, 2 : 1 and 2 : 3. A few 1 : 3 and 2 : 5 complexes were also isolated. Jander and Gunther[2] while studying the solvent properties of fused $AsBr_3$ reported the formation of solvates like $Me_4NBr.\ AsBr_3$, $Et_4NBr.\ AsBr_3$ etc. In the present work the reactions of $AsBr_3$ with a few amine hydrobromides were studied in aqueous hydrobromic acid medium. The complexes obtained were of the types, 1 : 1 and 2 : 3 (arsenic tribromide : amine hydrobromide). Their preparation, properties and characterization are reported in the present article.

Preparation : The preparative method consisted in mixing a solution of arsenic tribromide with that of amine hydrobromide both in aqueous hydrobromic acid medium. Solution of arsenic tribromide was prepared either by dissolving arsenic tribromide or arsenic trioxide in hydrobromic acid.

Arsenic tribromide was prepared by refluxing a mixture of arsenic trioxide, sulphur and bromine[3] at 80° ; it was purified by distillation. Arsenic tribromide was then dissolved in dilute hydrobromic acid to yield the desired solution. Arsenic trioxide was heated with a slight excess of 48% hydrobromic acid than required by the stoichiometry of the equation $As_2O_3+6HBr=AsBr_3+3H_2O$. The mixture was cooled and filtered to remove the undissolved arsenic trioxide. Solutions of amine hydrobromides were prepared by mixing 48% hydrobromic acid with respective amines, the amount of hydrobromic acid used in each case was in slight excess to that required for complete conversion of amine to amine hydrobromide.

The solutions of amine hydrobromide and arsenic tribromide were mixed in the molar ratio of 10 : 1 (amine hydrobromide : arsenic tribromide). In some cases a precipitate appeared immediately, in others after a while (~2 hr) and yet in others after long standing (~8 hr). The solids so obtained were filtered and washed with acetone. They were then recrystalized from 1 : 1 (by volume) mixture of acetone and isopropanol. The pyridinium compound could not be recrystallized because of its insolubility in the solvent mixture. The crystals were washed with diethylether and dried in vacuum desiccator.

Analysis :

The compounds were analysed for arsenic and bromine. The samples were dissolved in water (they hydrolysed in water yielding a clear solution containing arsenious acid, hydrobromic acid and amine hydrobromide). Aliquot of the solution was titrated with standard iodine solution for determining the arsenic content[4]. Arsenic was also determined gravimetrically by precipitating and weighing[5] as As_2S_3. Bromine was determined in the above solution by potentiometric titration with standard silver nitrate solution after acidification with dilute nitric acid[6]. The results on nitrogen content of the samples were obtained from microanalytical laboratory, C.D.R.I., Lucknow (India). Carbon and hydrogen could not be determined in these samples due to interference from arsenic (as per report of the microanalytical laboratory). The analytical results are reported in Table 1.

Physical Appearance :

All the solids were crystalline. Some of them were clear white and some had a yellowish tinge. Others were light to dark grey in colour.

Solubility :

Most of the compounds were soluble in solvents like nitromethane, acetone and isopropanol, but were insoluble in solvents like carbon tetrachloride. benzene and toluene.

Melting Points

The compounds did not show sharp melting points but had a range of about 2°. The melting point are shown in Table 1. The melting point

* Correspondence to be addressed to.

TABLE—1 ANALYTICAL RESULTS (in%) AND MELTING POINTS

Compounds	Elements	Calculated	Found	M.P. °C.
1. Dimethylammonium tetrabromoarsenate(III)	N	3.97	4.20	192-194
	As	16.58	16.92	
	Br	72.57	71.97	
2. N-dipropylammonium tetrabromoarsenate(III)	N	2.60	1.90	98-100
	As	15.07	15.70	
	Br	64.43	64.06	
3. Quinoliniumtetrabromoarsenate(III)	N	2.66	2.52	157-160
	As	14.26	14.15	
	Br	60.96	60.30	
4. Tris(n-butylammonium) nonabromodiarsenate(III)	N	3.84	3.50	157-160
	As	13.72	13.55	
	Br	65.80	65.76	
5. Tris(methylammonium) nonabromodiarsenate(III)	N	4.34	3.87	267-268
	As	15.51	15.50	
	Br	74.54	74.22	
6. Tris(allylammonium)nonabromodiarsenate(III)	N	3.09	3.05	150-155
	As	14.35	14.40	
	Br	69.17	69.45	
7. Benzylammonium tetrabromoarsenate(III)	N	2.78	—	128-130
	As	14.89	15.15	
	Br	63.63	63.34	
8. Tris(pyridinium) nonabromoarsenate(III)	N	3.78	5.13	128-130
	As	13.49	14.00	
	Br	64.87	64.76	
9. Tributylammonium tetrabromoarsenate(III)	N	2.41	—	173-175
	As	12.89	12.75	
	Br	55.08	55.00	

of quinolinium tetrabromoarsenate(III) was reported to be 148°(1) but in the present work it was found to be 157-159°.

Chemical Reactivity

Bromoarsenates (III) are stable at room temperature in open. They are hydrolysed by water to produce a clear solution containing arsenious acid, hydrobromic acid and amine hydrobromides.

Discussion

The reported methods of preparation of bromoarsenates[a] required either the use of fused $AsBr_3$ or the use of non-aqueous solvent[1]. The present method is a simple one requiring only arsenic trioxide, hydrobromic acid and various amines as starting material. It may be remarked at the very start though these compounds have been referred to as bromoarsenates(III), no direct evidence has been adduced to show that bromoarsenate ions like $AsBr_4^-$ are present in these solids. In the case of a similar compound namely $Cs_3As_2Cl_9$ it has been shown by X-ray crystallographic analysis[7] that the lattice does not contain discrete As_2Cl_9 ions but is composed of Cs^+, Cl^- and discrete $AsCl_3$ groups. $AsCl_3$ groups are embedded between Cs^+ and Cl^- in such a way that all atoms are in approximately close packing. Thus this compound may be assumed to be double salt, $3CsCl.2AsCl_3$. It is likely that the compounds reported in the present work are also similar double salts.

However, recently evidence has been obtained to prove the existence of tetrabromoarsenate ion, $AsBr_4^-$. It has been shown by Raman and i.r. spectroscopy that tetra *n*-butylammonium tetrabromoarsenate, $(n\text{-}Bu_4N)\ AsBr_4$ contains $AsBr_4^-$ anion of C_{2v} symmetry both in solid and solution (in nonaqueous solvents[8]. In view of the similarity of the cations reported in the present work with that of reported earlier[8] it may be assumed that the 1 : 1 complexes do contain $AsBr_4^-$ ions.

It is noteworthy that the compounds formed in the present work are either tetrabromoarsenates (1 : 1) or nonabromodiarsenates (2 : 3). No penta- or hexabromoarsenates were obtained even though the ratio (arsenic tribromide : amine hydrobromide) was always 1 : 10 i.e. larger excess of amine hydrobromide was present in every preparation than required for the highest coordination of arsenic, say six, to produce $AsBr_6^{3-}$. Such a behaviour gives support to the view that the 1 : 1 complex contains $AsBr_4^-$ and that penta- and hexabromoarsenates are not formed because of the steric factor—the larger size of bromine and smaller size of arsenic resulting in too much crowding around arsenic. A few 1 : 2 and 1 : 3 compounds are reported by Popov[1] but they may be double salts of arsenic tribromide and amine hydrobromide and may not contain bromoarsenate anions. However they may even turn out to be double salts containing tetrabromoarsenate and amine hydrobromide e.g. A_2AsBr_5 (A=substituted ammonium cation) may be represented as $AAsBr_4.ABr$ and A_3AsBr_6 as $AAsBr_4.2ABr$.

The nonabromodiarsenates (III) may have structures similar to that of $Cs_3As_2Cl_9$ and $AsBr_3$ may be present as such in the lattice of protonated amine cations and bromide anions.

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Some Substituted Thioureas and Their Reactions with the Platinum Metal Ions

S. C. SHOME, M. MAZUMDER, P. K. HALDAR and D. K DAS*

Chemical Laboratory, Presidency College, Calcutta

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Some substituted thioureas have been prepared and their reactions with the platinum metal ions have been studied. The results indicate that the thiourea derivatives, N-phenyl-N'-acetyl thiourea, N-α-pyridyl-N'-benzoyl thiourea and N-α(5-bromopyridyl)-N'-benzoyl thiourea are potential analytical reagents for the determination of those metals.

A survey of literature reveals that amongst the different classes of sulphur containing ligands, thiourea[1] and substituted thioureas[2] play an important role in the determination of platinum metals. Attempts[3] were made to improve upon the selectivity and sensitivity of the colour reactions of thiourea with the platinum metal ions substituting the hydrogen atoms of the reagent by various groups. Although thiourea and alkyl, aryl or -NHR substituted thioureas offer sensitive colour reactions with the platinum metals, they, however, suffer from lack of selectivity and their metal complexes are also unsuitable for gravimetry by direct weighing.

It is considered that the introduction of an acyl group on one of the nitrogen atoms of the thiourea molecule may yield a better reagent for analytical purposes. The availability of an extra oxygen atom as donor in addition to nitrogen and sulphur in the thiourea molecule may increase the potentiality of the ligand towards complexation. Further the substitution of a hydrogen atom of the second nitrogen atom of the thiourea molecule with a pyridyl group, instead of an alkyl or aryl group, may enhance the basic character of the ligand resulting in an increased solubility of the ligand in polar solvents.

In view of the above considerations, the following reagents have been prepared in the present research and their analytical properties have been studied thoroughly.

I. N-phenyl-N'-benzoyl thiourea.
II. N-phenyl-N'-acetyl thiourea.
III. N-(2-nitrophenyl)-N'-benzoyl thiourea.
IV. N-(2-nitrophenyl-N'-acetyl thiourea.
V. N-(4-nitrophenyl)-N'-benzoyl thiourea.
VI. N-(4-nitrophenyl)-N'-acetyl thiourea.
VII. N-α-pyridyl-N'-benzoyl thiourea.
VIII. N-α-pyridyl-N'-acetyl thiourea.
IX. N-α-(5-bromopyridyl)-N'-benzoyl thiourea.
X. N-α-(5-bromopyridyl)-N'-acetyl thiourea.
XI. N-α-pyridyl-N'-(3-nitrobenzoyl) thiourea.
XII. N-α-pyridyl-N'-(4-nitrobenzoyl) thiourea.

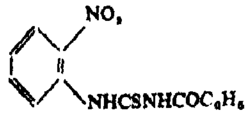
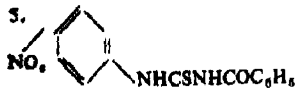
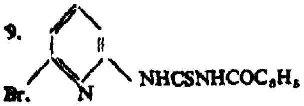
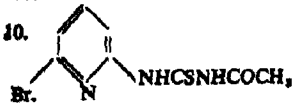
*Present Address: Central Ground Water Board, E. R., 24, Park Street, Cal-16.

Experimental

Preparation and Analysis of Thiourea Derivatives: General method of preparation: All the acyl substituted thioureas of the type $R\text{-}NH\text{-}\underset{\underset{S}{\|}}{C}\text{-}NH\text{-}\underset{\underset{O}{\|}}{C}\text{-}R'$ [R=Phenyl, nitrophenyl, pyridyl, bromopyridyl; R'=Benzoyl, acetyl, nitrobenzoyl] were prepared by the following general procedure. Ammonium thiocyanate (0·1 mole) was disolved in acetone and 0·1 mole of the respective acylating agent (R'.CO. Cl) was added slowly with constant shaking. The mixture was refluxed for 15 minutes on a hot water bath, cooled to room temperature and filtered. A solution of 0.1 mole of the corresponding amine ($R.NH_2$) in acetone was slowly added to the filtrate and mixed well with shaking. The mixture was refluxed for 10 minutes on a hot water bath and most of the acetone was removed by distillation. The residue was added slowly in crushed ice taken in a beaker with constant stirring until the reagent solidified. The crude reagent was filtered and recrystallised from ethanol.

The results of analysis of the thiourea derivatives are given in Table-1. The nitrogen content was determined by Kjeldahl's method (Reagent Nos. 1 to 6) and by Dumas method (reagent Nos. 7 to 12). Sulphur and bromine were estimated gravimetrically as barium sulphate and silver bromide respectively after decomposition of the compounds with sodium peroxide.

TABLE 1

Ligand	Molecular formula	M.P.	% Nitrogen Calc.	% Nitrogen Found	% Sulphur Calc.	% Sulphur Found	% Bromine Calc.	% Bromine Found
1. 	$C_{14}H_{12}N_2OS$	150°	10.93	10.89	12.5	12.46	—	—
2. 	$C_9H_{10}N_2OS$	174°	14.43	14.42	16.49	16.50	–	–
3. 	$C_{14}H_{11}N_3O_3S$	131°	13.95	13.90	10.63	10.61	—	—
4. 	$C_9H_9N_3O_3S$	163°	17.57	17.50	13.38	13.37	—	–
5. 	$C_{14}H_{11}N_3O_3S$	152°	13.95	13.92	10.63	10.65	—	—
6. 	$C_9H_9N_3O_3S$	177°	17.57	17.46	13.38	13.39	—	—
7. 	$C_{13}H_{11}N_3OS$	144°	16.34	16.35	12.45	12.42	—	—
8. 	$C_8H_9N_3OS$	158°	21.53	21.51	16.41	16.40	—	—
9. 	$C_{13}H_{10}N_3OSBr$	160°	12.50	12.52	9.52	9.50	23.80	23.81
10. 	$C_8H_8N_3OSBr$	182°	15.32	15.30	11.67	11.65	29.19	29.18
11. 	$C_{13}H_{10}N_4O_3S$	120°	18.54	18.52	10.59	10.60	–	–
12. 	$C_{13}H_{10}N_4O_3S$	180°	18.54	18.55	10.59	10.57	–	—

Results and Discussion

Metal Chelates and their Properties

(a) *Metal chelates of N-α-pyridyl-N'-benzoyl thiourea (VII)* : The ligand possesses excellent chelating ability with all the platimum metals and the properties of the chelates are summarized in the Table-2. The emperical formulae of the complexes were assigined by the mole-ratio method as described by Meyer and Ayres[4].

(iii) The chelates are of definite composition and thermally stable.

(iv) The complexes are of different colour and easily extractable in organic solvents.

(v) The deep coloured extracts of the complexes in ethanol-chloroform mixture are stable for more than 24 hours.

(b) *Metal chelates of N-α-(5-bromopyridyl)-N'-benzoyl thiourea (IX)* : The conditions for the reactions of the ligand with the platinum metals and the properties of the chelates formed are given in the Table-3.

TABLE-2 CHELATES FORMED BY N-α-PYRIDYL-N'-BENZOYL THIOUREA WITH PLATINUM METALS

Metal ion	Condition of complex formation	Colour of complex	Extractable in	Ligand to metal ratio in the complex	M.P. of chelate
Ru(III)	Hot acetate buffer medium, *p*H 3.7-5.2	Deep brown	Ethanol chloroform mixture	2 : 1	170°
Rh(III)	Hot acetate buffer medium, *p*H 3.5-5.5	Brown	-do-	3 : 1	162°
Pd(II)	Dil. hydrochloric acid, 1.6(N)-0.08(N)	-do-	-do-	1 : 1	158°
Ir(III)	Hot acetate buffer medium, *p*H 4.2-5.86	Orange yellow	-do-	3 : 1	172°
Os(VI)	Hot acetate buffer medium, *p*H 3.1- 6.2	Dark green	-do-	2 : 1	260°
Pt(IV)	Hot acetate buffer medium, *p*H 4.06-6.2	Yellow	-do-	2 : 1	160°
Pt(II)	Hot and dilute hydrochloric acid, 0.5(N) to 2.01(N)	Brown	-do-	1 : 1	195°

TABLE-3 CHELATE FORMED BY N-α-(5-BROMOPYRIDYL)-N'-BENZOYL THIOUREA WITH THE PLATINUM METAL IONS.

Metal ions	Condition for complex formation	Colour of complex	Extractable in	Ligand to metal ratio in complex
Ru(III)	Hot acetate buffer medium, *p*H 4.7-6.4	Deep brown	Ethanol-chloroform mixture	2 : 1
Rh(III)	Hot acetate buffer medium, *p*H 6.2-7.1	Deep yellow	-do-	3 : 1
Pd(II)	Cold acetate buffer medium, *p*H 3.8-6.1	Deep brown	-do-	1 : 1
Os(VI)	Hot acetate buffer medium, *p*H 2.24-3.2	Dark green	-do-	2 : 1
Ir(III)	Hot acetate buffer medium, *p*H 4.9-6.2	Orange yellow	-do-	3 : 1
Pt(IV)	Hot acetate buffer medium, *p*H 2.02-2.6	Deep yellow	-do-	2 : 1

N-α-pyridyl-N'-benzoyl thiourea is likely to serve as an ideal analytical reagent for both the gravimetric and spectrophotometric purposes due to the following reasons :

(i) The reagent is appreciably soluble in hot water whereas the chelates are insoluble and they can be easily freed from excess reagent.

(ii) The complex formation reactions could be made selective in most of the cases by proper control of *p*H, temperature etc.

The reagent cannot be recommended for the gravimetric purpose due to its insolubility in water. However, it could be employed for the spectrophotometric determination of the platinum metals due to following reasons :

(i) The complexes are formed under different conditions of the reaction media.

(ii) The complexes are highly coloured and easily extractable in organic solvents.

(iii) The colour of the ethanol-chloroform extracts of the complexes are stable for more than 24 hours.

(c) *Metal chelates of N-phenyl-N'-acetyl thiourea (II)* : The preliminary investigation of the reactions between the platinum metal ions and the reagent indicate that the chelates are partly soluble in water. Palladium (II), rhodium (III) and platinum (IV) produce similar colour reactions with the ligand under similar conditions of acidity. On the other hand the colour reactions with ruthenium (III) and osmium (VI) in 50% ethanol seem to be selective.

The remaining ligands (I, III, IV, V, VI, VIII, X, XI and XII) can not be employed for the determination of the platinum metals due to the following disadvantages :

(i) Most of them are insoluble in water.

(ii) Poorly soluble in ethanol.

(iii) The chelates formed are of hydrated in nature and partly soluble in water.

(iv) The chelation takes place under the same condition of acidity.

(v) Most of the complexes cannot be extracted completely with the common organic solvents.

The preliminary studies of the reactions between the twelve substituted thioureas and the platinum group of metals were undertaken with a view to examine the possibility of application of those reagents in preference to thiourea itself. Among those, N-phenyl-N'-acetyl thiourea produces fairly sensitive and selective colour reactions with osmium (VI) and ruthenium (III) but it is unsuitable for the gravimetry of these platinum metals. The reagent N-α-pyridyl-N'-benzoyl thiourea seems to possess potentiality as an ideal analytical reagent for the gravimetric and spectrophotometric determination of the noble metals. N-α-(5-bromopyridyl)-N'-benzoyl thiourea is a more sensitive reagent for the colorimetry of the platinum metals, especially of osmium (VI). The compound is, however, not suitable for the gravimetric determination of these metals. These three thiourea derivatives are found to be quite sensitive and more selective than thiourea in the analysis of platinum metals as can be seen from Table 4.

TABLE-4 COMPARISION OF ANALYTICAL PROPERTIES OF THIOUREA AND SOME SUBSTITUTED THIOUREAS.

Reagents	Determination of Ruthenium		Determination of Osmium		Determination of Palladium	
	Range (ppm)	Interferences	Range (ppm)	Interferences	Range (ppm)	Interferences
1. Thiourea	2-15	Rh, Ir, Pt & Os	5-50	Pd, Ru	0.8-24	*
2. N-phenyl-N'-acetyl thiourea	1-20	None	2-25	Rh		
3. N-α-pyridyl-N'-benzoyl thiourea	1-8	None	0.5-25	None	0.5-12	None
4. N-α-(5-bromo-pyridyl)-N' benzoyl thiourea	0.5-5	None	6.0-30	None	0.3-5	None

* No quantitative data available.

Acknowledgement

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Benzoyl-*m*-nitroacetanilide as a Gravimetric Reagent for Manganese(II)

SANAT KUMAR MANDAL and JOYTIRMOY DAS*

Chemistry Department, The University of Burdwan, Burdwan-713104

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Manganese(II) has been quantitatively precipitated with benzoyl-*m*-nitroacetanilide and weighed as $Mn(C_{15}H_{11}O_4N_2)_2$ after drying at 120°. The *p*H of precipitation is 6.5-8.0. The presence of Ag^+, Tl^+, citric acid, sulphosalicylate, tartrate and iodide do not interfere in the determination. Citrate has been used to mask Cu^{2+}, Cd^{2+}, Zn^{2+} and VO^{2+}, sulphosalicylic acid for Ni^{2+}, Co^{2+} and Fe^{3+}, tartrate for Pb^{2+}, Bi^{3+}, Al^{3+}, Cr^{3+}, UO_2^{2+} and WO_4^{2-} and iodide for Hg^{2+} in the quantitive separation of manganese from these ions. The relative standard deviation is ±0.21%.

THE bonding of manganese(II) is mainly ionic and the tendency of formation of complexes with neutral ligands including oxygen containing anions is very little[1]. Thus, there are only very few organic reagents like 8-quinolinol[2], quinaldinic acid[3] and thioanilide with which maganese(II) can be determined and oxidation to permanganate is more convenient for this purpose.

However, benzoyl-*m*-nitroacetanilide which has been first used as a gravimetric reagent for beryllium[5] and subsequently for several other metal ions has now been successfully used in the determination of mangansese(II) from near neutral solutions.

Experimental

Benzoyl-m-nitroacetanilide : The reagent was prepared in the laboratory[6] and a fresh solution containing 0.18-0.22 g of it in 15 ml aqueous ethanol was prepared before use.

Manganese (II) Solution : Manganese (II) chloride (BDH) was dissolved in dilute hydrochloric acid and suitably diluted. The metal content was determined titrimetrically after oxidation to permanganate.

All the other chemicals used were of A. R. or G. R. grade.

Apparatus :

A battery operated bench model Cambridge *p*H-meter was used to measure the acidity and a photorecording Metriplex Derivatograph OD-102 (Hungary) was used for the thermogravimetric studies. Magnetic susceptibility was measured in a modified electromagnetic microbalance[7].

Procedure :

An aliquot of the stock solution containing 6 to 16 mg of manganese diluted to 150 ml with water was heated almost to boiling after the *p*H was adjusted to 4.0-4.5 with sodium acetate (5%) solution. The reagent solution was added slowly with stirring. The yellow manganese(II)-benzoyl-*m*-nitroacetanilide complex was formed instantly on raising the *p*H to 6.5-8.0 with aqueous 2*N* ammonia. The precipitate was filtered through a sintered glass crucible of fine porosity after digesting on a hot water bath for 20 to 30 minutes, washed first with hot water (70-80°) and finally with 30 ml of 20% ethanol. This was weighed as $Mn(C_{15}H_{11}O_4N_2)_2$ after drying at 120°. The factor of the metal in the complex was 0.0884. The results of these determinations are given in Table 1.

TABLE—1 DETERMINATION OF MANGANESE(II)

Mn taken (mg)	Wt. of complex (mg)	Mn found, (mg)	Rel.error. (%)
6.33	72.0, 71.6	6.36, 6.32	+0.47, −0.15
10.56	119.5, 119.3	10.56, 10.54	nil −0.18
16.88	190.8, 191.2	16.86, 16.90	−0.11, +0.11

Separation from Diverse Ions :

When manganese(II) was precipitated from solutions containing other metal ions, a suitable masking agent, e.g. citric acid (1 g), sulphosalicylic acid (0.5 g), sodium potassium tartrate (1 g) or potassium iodide (0.1 g) was added before the addition of the reagent and the *p*H was finally adjusted between 7.5 and 8.0 otherwise the procedure was same as described above. Separation of manganese from reasonable amounts of Ag^+ or Tl^+ was possible using benzoyl-*m*-nitroacetanilide as the precipitant. However, 1 g of citric acid was used to mask Cu^{2+} Cd^{2+}, VO^{2+} and Zn^{2+} and 0.5 g sulphosalicylic acid

for Fe^{3+}, Co^{2+} and Ni^{2+}. Manganese was precipitated in the presence of Pb^{2+}, Bi^{3+}, Al^{3+}, Cr^{3+}, UO_2^{2+} and WO_4^{2-} using 1 g of sodium potassium tartrate as the masking agent. Hg^{2+} was masked with 0.1 g of potassium iodide. In these experiments generally the divirse ions taken were about four times the amount of manganese (II). However, in case of bismuth and aluminium the amounts were lower as otherwise the relative error was beyond $\pm 0.5\%$. The results of these separations are given in Table 2.

metric (DTG) curves recorded have been presented in Figure 1.

The complex was found to be stable upto 220°, when a rapid exothermic decomposition took place and a loss of about 39% in weight was recorded. At 300° another exothermic change was noted, which was somewhat less rapid than the first one. The oxidation to the oxide stage was complete at 500°. The calculated loss for converstion to MnO_2 was 86%, while the experimental value (85%) was

TABLE—2 SEPARATION OF MANGANESE FROM DIVERSE IONS MANGANESE(II) TAKEN : 10.56 MG

Diverse ions (mg)	Masking agent	Wt. of complex (mg)	Mn found (mg)	Rel. error (%)
Ag^{+}, 40	-	119.6, 119.3	10.57, 10.54	+0.09, −0.18
Tl^{+}, 40	-	119.4, 119.5	10.56, 10.56	−0.09, nil
Hg^{2+}, 40	a	119.4, 119.7	10.55, 10.58	−0.09, +0.18
Cu^{2+}, 40	b	119.6, 119.1	10.57, 10.52	+0.09, −0.37
Cd^{2+}, 40	b	119.5, 119.2	10.56, 10.53	nil, −0.28
Zn^{2+}, 40	b	119.5, 119.4	10.56, 10.55	nil, −0.09
VO^{2+}, 40	b	119.2, 119.4	10.53, 10.55	−0.28, −0.09
Ni^{2+}, 40	c	119.7, 119.9	10.58, 10.60	+0.18, +0.37
Co^{2+}, 40	c	119.8, 119.4	10.59, 10.55	+0.28, −0.09
Fe^{3+}, 40	c	119.5, 119.2	10.56, 10.53	nil, −0.28
Pb^{2+}, 40	d	119.3, 119.7	10.54, 10.58	−0.18, +0.18
Bi^{3+}, 20	d	119.7, 119.8	10.58, 10.59	+0.18, +0.28
Al^{3+}, 30	d	119.6, 119.5	10.57, 10.56	−0.09, nil
Cr^{3+}, 40	d	119.1, 119.4	10.52, 10.55	−0.37, −0.09
UO_2^{2+}, 40	d	119.7, 119.4	10.58, 10.55	+0.18, −0.09
WO_4^{2-}, 40	d	119.9, 119.7	10.60, 10.58	+0.37, +0.18

(a) Potassium iodide, (b) Citric acid, (c) Sulphosalicylic acid, (d) Sodium potassium tartrate

Results and Discussion

Properties and Composition of the Complex :

The yellowish coloured complex is practically insoluble in ethanol, though soluble in acetone, isobutylmethylketone, chloroform and tributylphosphate. The pure complex was analysed for nitrogen by Kjeldahl's method (using glucose for the reduction of nitro group) and for manganese. The experimental results, Mn (calc. 8.84%, found 8.90, 8.81%) and N(calc. 9.01%, found 8.91, 8.95%) indicated the formula to be $Mn(C_{15}H_{11}O_4N_2)_2$.

Magnetic Data :

The manganese(II)-bis-benzoyl-*m*-nitroacetanilide chelate was found to be paramagnetic. The molar magnetic susceptibility ($\xi_m = 12690 \times 10^{-6}$ cgs unit) and $\mu = 5.61$ B. M. was in agreement to the expected value.

Thermal Decomposition Studies :

The oven-dried (120°) sample of manganese(II)-benzoyl-*m*-nitroacetanilide complex (100 mg) with Al_2O_3 was subjected to heating at the rate of 12° per min. in air. The weight change (TG), differential thermal analysis (DTA) and differential thermogravi-

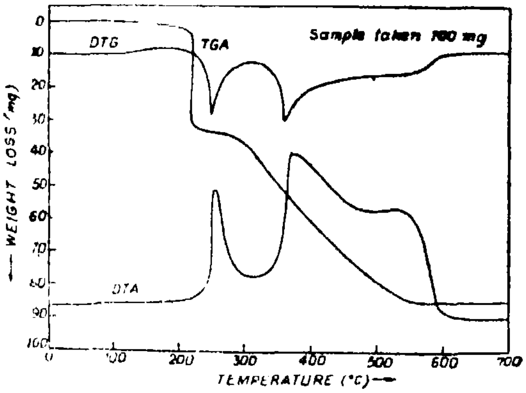


Fig. 1 Thermal decomposition curves of Manganese(II)-Benzyl-*m*-nitroacetanilide.

slightly lower. This may be due to the formation of small amount of some other oxide. The initial part of the TG curve was slanting which is probably due to adhered moisture as no change was indicated in the corresponding part of the DTA curve.

Effect of pH and Concentration of the Reagent :

Experiments on the precipitation of manganese from solutions adjusted to varying *p*H showed that the process was quantitative in the range 6.5 to 8.0.

The precipitation of manganese was carried out at fixed *p*H value (7.0) using varied amounts of the reagent, maintaining all other conditions identical. For the complete precipitation at least three times the reagent thoretically calculated was required.

Effect of Sequestering Agents :

The determination of manganese (II) was possible in the presence of citric or ascorbic acid, sulphosalicylic acid, tartrate and potassium iodide. However, the precipitation was prevented in the presence of Mg-EDTA and fluoride tartaric acid.

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A Study of the Effect of Dry Oxygen on Alkylthio- and Alkoxyantimonite

SHUVENDU CHATTERJEE

Chemical Laboratories, Tata College, Chaibasa-833202, Dist. Singhbhum, Bihar, (Ranchi University)

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Soluble and volatile alkylthioantimonite $Sb(SR)_3$ has been found to undergo decomposition in contact with dry oxygen to yield volatile dithiol RSSR alongwith an insoluble and non-volatile mixture of Sb_4O_8 and $(RS)_3SbO$ in the ratio 3.5 : 1, as the final products of decomposition, whereas antimony trialkoxide $Sb(OR)_3$ remain inactive towards dry oxygen. An endevour has been made to focus on the mode of decomposition of the alkylthio derivatives with respect to the inertness of alkoxyantimonites towards dry oxygen. The decomposition of the alkylthio antimonites proceeds probably through the following two plausible steps involving SR free radical alongwith the formation of dithiol RSSR :

$$2(RS)_3Sb+O_2 \xrightarrow{\text{dry benzene}} 2(RS)_3SbO\downarrow$$

$$4(RS)_3SbO+O_2 \xrightarrow{\text{dry benzene}} Sb_2O_8\downarrow+6\ RSSR\uparrow.$$

IN comparison to metal-oxygen-carbon bonded metal aloxides[1-4] M(OR)n, alkylthio derivatives[5-7] M(SR)n, having metal-sulphur-carbon bonds, are comparatively of recent interest. While carrying out the isolation and studies of number of alkylthioantimonites[7,8] an interesting behaviour was observed on storage of these alylkthio derivatives $Sb(SR)_3$[7,8]. White solids were found to separate out slowly from these colourless and volatile alkylthioantimonites[7,8], even when they were kept in a stoppered flask. In contract to the soluble and volatile nature of these alkylthio derivatives[7,8] these separated solid masses were found to be non-volatile and insoluble in the inert organic solvents like benzene but tend to redissolve in the medium of parent thiol on heating. Further experiments showed that the rate of decoposition of the liquid thioantimonites appear to become almost negligible under vacuum or in an atmosphere of nitrogen. From this, it appears that the atmospheric oxygen played a role in these decompositions occuring during storage and hence the reaction of alkylthioantimonite[7,8] with dry oxygen was investigated.

To establish a comparative survey of Sb-S-C bonded thiol derivatives[7,8] with alkoxides possessing Sb-O-C bonds towards the effect of dry oxygen, the similar study has also been extended[9-11] to antimony tri-ethoxide $Sb(OEt)_3$.

Results and Discussions

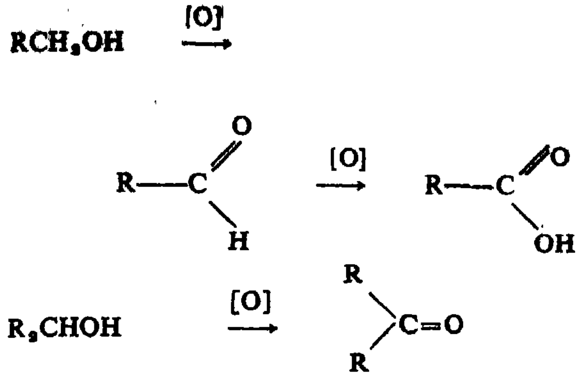
An exthormic reaction was observed alongwith the gradual separation of insoluble solid, when dry oxygen was passed under rigorous moisturefree condition into a benzene solution containing butylthioantimonite[7,8] and the dry oxygen was passed for about 10 hours. After filteration and drying, the separated insoluble solid was found on analysis to be a probable mixture of Sb_4O_8 and $(BuS)_3SbO$ in the ratio of 3.5 : 1. The filtrate gave of BuSSBu on disillation. Further passage of dry oxygen through a suspension of the insoluble solid in benzene did not produce any notioceable analytical change. The results have been summarised in the flow sheet No. 1.

When a benzene solution containing ethoxyantimonite[7,9-11] $Sb(OEt)_3$ was treated with dry oxygen under exactly similar condition any physical or chemical change did not take place. (Vide flow sheet No. 2).

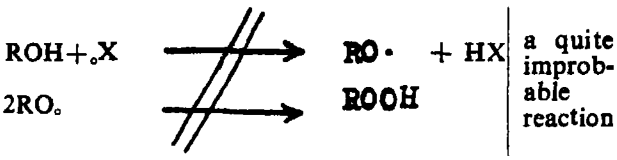
Thus, it was observed that butylthioantimonite[7,8] was found to be sensitive even to dry oxygen to yield oxide and dibutyldisulphide BuSSBu, whereas the antimony trithoxide[7,8,10,11] has been found to be quite stable towards dry oxygen. The more easily oxidisable nature of thiols and alkylthio groups, with respect to alcohols or alkoxy groups may be the probable cause of the reactivity of alkylthioantimonites[7,8] in comparison to alkoxyantimonites,[7,9-11] towards dry oxygen.

Thiols and alcohols behave quite differently towards oxidising agents. Oxidation of alcohols proceeds, in general, with an increase in the oxidation level of carbon rather than that of oxygen,

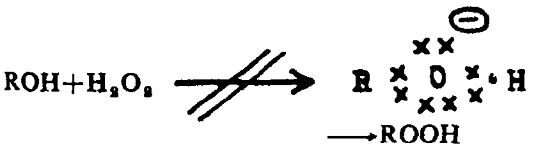
hence there is formation of carbonyl groups, but not peroxides :



This is due to the fact that O—H (111 Kcal) in alcohol is strong bond and needs a powerful oxidising agent to achieve one-electron oxidation of oxygen by removing a hydrogen atom from the hydroxyl group of an alcohol :



Apart from it, the hydrogen oxygen of an alcohol is not found to accept an oxygen atom from mild oxidising agents like hydrogen peroxide :



In the oxidation of thiols,

(i) Sulphur is more easily oxidised than carbon.
(ii) the compounds in which sulphur is in higher oxidation state, are found to be quite stable.

(iii) as the strength of S—H bonds (83 Kcal) is considerably less than that of O—H bonds (111 Kcal), the reaetion mechanisms, which are unfavourable for alcohols, are found to be quite favourable for thiols.

Thus, it is observed that the oxidation of thiols, with a mild oxidising agents like atmospheric oxygen produce dialkyldisulphide RSSR probably with the formation of alkylthio radicals :

$$R{-}S{-}H + [O] \rightarrow R{-}S. + H[O]$$
$$2\ RS. \rightarrow R{-}S{-}S{-}R \quad \text{dialkyldisulphide}$$

Hence the decomposition of the alkylthioantimonites[7,8] proceeds probably through the following two plausible steps by a mechanism[7,8,12] involving SR free radical alongwith the formation of dithiol RSSR :

$$2(RS)_3Sb + O_2 \xrightarrow{\text{dry benzene}} 2(RS)_3SbO \downarrow \quad \ldots\ldots(i)$$

$$4(RS)_3SbO + O_2 \xrightarrow{\text{dry benzene}} Sb_2O_3 \downarrow + 6RSSR \uparrow \quad \ldots\ldots(ii)$$

As a matter of fact, the, presence of $(BuS)_3SbO, Sb_2O_3$ and BuSSBu have been detected in the decomposed product. Probably due to the insoluble nature of both $(BuS)_3SbO$ and Sb_2O_3 in the medium of dry benzene, the second step of the reaction does not proceed to completion.

Experimental

Butylthioantimonite[7,8] was prepared by the reaction of anhydrous antimony trichloride with butanethiol in presence of gaseous ammonia[7,8]. Ethoxyantimonite[7,9-11] was prepared by the reaction of anhydrous antimony trichloride with sodium ethoxide in the molar ratio 1 : 3 as described[7,9-11]. Both of these derivatives have been isolated under rigorous moisturefrre condition[7] and were purified before use by distillation under vacuo[7]. [B.pts, $Sb(OEt)_3$ 94-5/10.0, and $Sb(SBu)_3$ 160/0.3 respectively].

The trivalant antimony present in the butylthioantimonite[7,8] was estimated by standard potassium bromate solution after decomposing the thioderivative[7,8] with bromine in the hydrochloric acid medium as described[7,8,13]. In ethoxyantimonite[7,9-11] antimony(III) was determined by the similar method[7,8,13] after dissolving the compound in the medium of hot hydrochloric acid. In the insoluble residue obtained after the decomposition of alkylthio derivative,[7,8] the total metal content [i.e. antimony (III)+antimony(V)] was found out by the above mentioned method[7,8,13] after digesting the residue with bromine in the medium of hot hydrochloric acid, and trivalent antimony was estimated by direct titration with standard potassium bromate[13] after digesting the solid in the medium of hot hydrochloric acid. Sulphur was estimitated gravimetrically[14] as $BaSO_4$.

An exothermic reaction was observed alongwith the gradual separation of insoluble solid, when dry oxygen was passed under rigorous moisturefree condition into a benzene (70 g) solution containing[7,8] 6.34 g of $Sb(SBu)_3$ [Analysis : Found : Sb, 31.1, S, 24.0 ; Calcd. for $Sb(SBu)_3$, Sb 31.3, S, 24.7%] and the dry oxygen was passed for about 10 hours. The separated residue was filtered and dried under vacuo to give a non-volatile and insoluble product (2.69 g) and was subjected to analysis. [Found : Sb^{III+V}, 69.1. Sb^{III} 60.4, S, 5.45. A mixture of Sb_2O_3 and $(BuS)_3SbO$ in the ratio 3.5 : 1 requires Sb^{III+V} 68.05, Sb^{III} 59.8, S, 6.75%] Dry Oxygen was further passed for about 40 hrs. through a suspension of 0.91 g of this insoluble residue in the medium of dry benzene under a rigorous moisturefree condition. 0.87 g of the insoluble product was recovred and was analysed. (Found : Sb^{III+V} 68.5 ; Sb^{III} 60.0, S, 5.2%).

The filtrate gave a 3.9 g of a colourless liquid b.pt. 117-118° on distillation at 20 mm Hg. and was analysed (Found : C, 52.9, H, 10.1, S, 35.2, Calcd. for BuSSBu ; C, 53.9, H 10.2, S, 35.9%). The results have been summarised in flow sheet No. 1.

No physical or chemical change was observed when dry oxygen was passed through a benzene solution (60g) containing 4.67 g of $Sb(OEt)_3$ [Analysis, Sb 47.6, Calcd. for $Sb(OEt)_3$; Sb.47.3%], and 4.35 g of liquid was recovered and was analysed Found : Sb, 47.9%, Calcd for $Sb(CEt)_3$: Sb, 47.3% (Vide Flow Sheet no. 2).

Flow Sheet No. 1

Effect of Dry Oxygen on $Sb(SBu)_3$

$Sb(SBu)_3$ (6.34 gms.)
in
benzone (70 gms.)

↓ dry oxygen was passed for 10 hrs.

(i) Exothermic reaction was observed.
(ii) Insoluble reside gradually separated out.

↓ filtered and the residue was washed with dry benzene

Left branch:

White residue (2.69 gms.) dried with the aid of vacum pump

↓ analysed

Calculated for a mixture of Sb_2O_4 and $SbO(SBu)_3$ in the molar ratio 3.5 : 1

Sb^{III+V}	69.1%
Sb^{III}	60.4%
S	5.45%

Analysis obtained :

Sb^{III+V}	68.65%
Sb^{III}	59.8%
S	6.75%

Right branch:

Filtrate

↓ excess of benzene removed with the aid of vacum pump

Colourless liquid (3.9 gms.) was obtained

↓ characterised

(i) b.pt. 117-118° at 20 mm. (Hg)

(ii) *Analysis* :

Found : C, 52.9% ; H, 10.1% ; S, 35.2%

Calcd. for BuSSBu ; C, 55.9% ; H,10.2% ; S, 35.9%

Flow Sheet No. 2

Effect of Dry Oxygen on $Sb(OEt)_3$.

$Sb(OEt)_3$ (4.67 gms.)
in
benzene (60 g.)

↓ dry oxygen was passed

No chemical or physical change was observed.

↓ excess of benzene was removed

Liquid (4.35 g.) was obtained

↓ analysed :

Found : Sb, 47.9%
Calcd. for $Sb(OEt)_3$; Sb, 47.3%.

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Thermal Studies on Oceanic Salts*

K. P. PATEL, O. K. SRIVASTAVA and N. N. SHARMA**

Central Salt & Marine-Chemicals Research Institute, Bhavnagar

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Successive evaporations of sea bittern after desalting of sodium chloride gives Sels Mixts between 34 and 36° Be', mixed salt between 36 and 38° Be' and leaves behind a mother liquor rich in magnesium chloride. The fraction, Sels Mixts, is a mixture of sodium chloride and magnesium chloride in widely varying proportions (NaCl 55.0 to 65.0% and $MgSO_4 7H_2O$ 35.0 to 45.0%). The differential thermal analysis of the Sels Mixts with NaCl 58% and $MgSO_4 7H_2O$ 42% were conducted and the results are presented in the paper. The thermographs obtained show two prominent endothermal effects at 225° and 625° which are neither due to epsom salt nor due to sodium chloride. On the other hand, these endothermal peaks are indicative of formation of astrakainite-a double sulphate of sodium and magnesium, $Na_2SO_4MgSO_4 4H_2O$, in the system.

THE salt is manufactured from seawater by solar evaporation. As the evaporation proceeds, fractions of salts are precipitated out. Bittern is the mother liquor obtained after desalting of brine and is 2% of the original volume of brine. Successive evaporation of bittern gives Sels Mixts between 34° and 36° Be', mixed salt between 36° and 38° Be' and leaves a mother liquor rich in magnesium chloride. Sels Mixts is a mixture of sodium chloride and epsom salt in widely varying proportions (NaCl 55-65% and epsom salt 35-45 %). It is the starting material for the manufacture of sodium sulphate. Sels Mixts is collected in the field in salt works and is stored for further processing.

Differential thermal studies of the system $NaClMgSO_4$, comprising of the two constituents of the Sels Mixts were carried out. Two Analar salts were mixed in the ratio as given below (the ratio is the same as actually found in samples of Sels Mixts obtained from our Experimental Salt Farm) :

NaCl	58.0 %
$MgSO_4 7H_2O$	42.0 %

Thermographs were taken of this synthetic mixture and also of the natural Sels Mixts and are given in Fig.1. Thermographs were recorded on the Sargent recorder model MR with chromel-alumel thermocouples. The sample and the reference material were packed in the holes of 8 mm dia and 12 mm depths drilled in the SS block. The sample holder with thermocouple were placed in the furnace vertically. The rate of heating was 10° per minute. Previously calcined Al_2O_3 was used as reference material and the temperature recorded were of this reference material. Representative thermographs recorded are given in the Figure 1 :

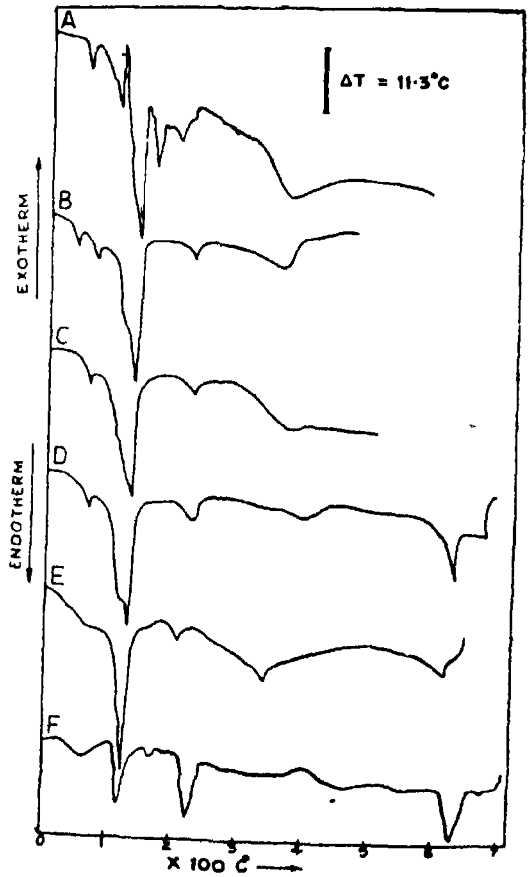


Fig 1

* The paper was presented at the convention of Chemists, 1975, held at Roorkee.
** For correspondence.

i) Curve, 'A' is for epsom salt, $MgSO_4\ 7H_2O$

ii) Curve 'B' is for synthetic mixture immediately after mixing.

iii) Curve 'C' is for synthetic mixture after 75 days of mixing.

iv) Curve 'D' is for synthetic mixture after 120 days of mixing.

v) Curve 'E' is for natural Sels Mixts collected from the salt works.

vi) Curve 'F' is for astrakainite.

The curves B, C, D & E show the following endothermal effects :

i) The first change in thermal energy is at 55°

ii) The second change begins at a temperature around 100° and is followed by a shoulder and a sharp peak at 138°.

iii) Very prominent effect is observed at 225°.

iv) The next effect is at 360°

v) The endothermal peak is recorded at 625° and finally the sample melts at 675°.

Suppose there is no reaction in the system and the two salts, i.e., NaCl and $MgSO_4\ 7H_2O$ maintain their individual identity, the characteristic endothermic effects of epsom salt should only have been observed. The energy changes in the epsom salt are : at 52° when heptahydrate melts ; at 97° when hexahydrate melts ; at 107° when tetrohydrate dehydrates ; at 117° when tetrahydrate dehydrates ; at 138° when trihydrates dehydrates ; at 184° when dihydrate dehydrates ; at 340° when kieserite dehydrates ; and finally, at 1124° when anhydrous magnesium sulphate melts.

These energy changes for epsom salt are collected from the literature[1-] and compare very favourably with the data recorded and presented in Cvrve 'A', Upto 138°, the energy changes in the curves B, C, D and E are comparable with those of epsom salt in the curve 'A' although at places the effects are overlapped and have resulted in shoulder formation. Beyond 138°, two important endothermal energy changes are recorded at 225° (Curve B, C, D, E & F) and at 625° (Curve D, E & F). These two effects can neither be ascribed to epsom salt nor to the sodium chloride the second salt of the system NaCl-$MgSO_4$. Sodium chloride[1] is not affected by heat at lower temperatures but melts at 800°. These two effects at 225° and at 625° are therefore indicative of the formation of some other salt.

In the liquid (solution) phase and under controlled conditions, the two salts, i.e., NaCl and $MgSO_4$ $7H_2O$ are known to undergo the following[3,4] reactions :

$$\text{I} \quad 2NaCl+2MgSO_4 \xrightarrow{H_2O} Na_2SO_4MgSO_4 4H_2O + MgCl_2$$

$$\text{II} \quad 2NaCl+MgSO_4 \xrightarrow{H_2O} Na_2SO_4.\ 10H_2O+MgCl_2$$

Under the experimental conditions, the first reaction seems to be more plausible (in solid state also) as the two salts react to form a natural mineral, astrakanite. In the second reaction, sodium sulphate decahydrate, $Na_2SO_4\ 10H_2O$, also known as Glauber's Salt, is formed. Glauber's Salt[8] melts at 32.4°, boils at 102°, undergoes polymorphic transformation at 240° and finally melts at 884°. In the curve B, C, D & E, no energy change is noticed either at 32.4° or at 240° and, therefore, it can be concluded that Glauber's Salt is not formed in the system.

Two sharp effects observed in the curves B, C, D and E at 225° and 625°, as referred to above, are characteristic of astrakanite and loweite (Curve F). The double sulphate of sodium and magnesium, astrakanite, becomes anhydrous at 225° by loosing remaining two molecules of water (the two having earlier been lost at 110°) and decomposes at 625°. The sensitivity[8] of these two thermal energy changes (one at 225° and the other at 625°) has been recorded as 2-5 mole %, on the lower side, in a mixture of salt system. Hence, it can be concluded that astrakainite is formed by the reaction of sodium chloride and epsom salt in the solid phase.

Coming to the endothermal effects beginning around 98°, followed by a shoulder and a Break at 138°, the first change in energy is recorded when the epsom salt melts (Curve B, C, D and E). The melt boils at 107°. It is around this temperature that astrakanite loses two molecules of water and forms loweite. All these effects are projected in the form of a shoulder which is actually cumulative effect of :

i) dehydration of hexahydrate, 98°

ii) dehydration of astrakanite, when it loses two molecules of water and forms loweite ; 110°

iii) dehydration of tetrahydrate, 117°

iv) melting of bischoffite, the second reaction product, formed during the reaction in equation I.

v) the final peak at 138° for the dehydration of $MgSO_4\ 3H_2O$

The endothermal effect observed around 350° is indicative of the complete dehydration of magnesium sulphate through kieserite. Anhydrous magnesium sulphate is formed at this stage.

It can be concluded that astrakanite is formed from the Sels Mixts on storing. Fresh samples do not show any such tendencies. However, much more

work on DTA, thermodynamic calculations and X-ray diffraction is necessary before a clear picture of the mechanism of reation can be fully established.

Acknowledgements

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Synthesis of Substituted Piperazinyl Semicarbazides and Thiosemicarbazide : as Possible Acetyl Cholinesterase(AChE) Inhibitors

ANIL K. SENGUPTA, K. C. AGARWAL and M. MUSHTAQ

Department of Chemistry, Lucknow University, Lucknow and
Industrial Toxicology Research Centre, Lucknow

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Some new N'-(N-aryl-N'-acetyl) piperazine-N⁴-aryl/alkyl Semicarbazide and Thiosemicarbazides have been synthesised as possible/Acetyl cholinesterase (AChE) Inhibitors, by the condensation of N-aryl N'-piperazine acetic acid hydrazide with aryl or alkyl isocyanate and aryl isothiocyanates.

PIPERAZINE derivatives have been shown to prosses diverse biological properties including antihistaminic[1], antimetic[2] and anticonvulsant[3,4] activities. Recent studies indicated the anticonvulsant activity of several thiosemicarbazides[5,6,7] and their ability to inhibit nicotinamide ademine dinucleotide (NAD) dependent oxidations. Furthermore anticonvulsants are known to inhibit acetyl cholinesterase[8,9]. This prompted us to synthesis the title compounds with the idea that the combined effect of the piperazine nucleus and >N-C(=S)- or >N-C(=O)→gr might confer much enhanced antiacecyl cholinesterase activity on these compounds.

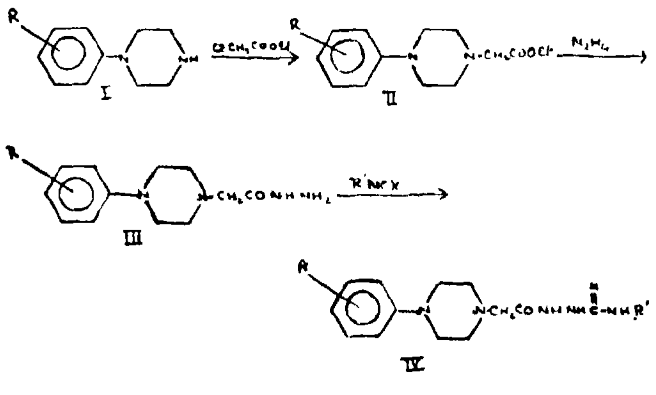
In all eighteen thiosemicarbazides and six semicarbazides have been prepared according to the tentative scheme given below. The structure given in compound IV is supported by infrared spectroscopy as the peaks of all vital functional groups tally with standard values reported in the literature. Absorption frequencies for -CONHNH, 2900 & 3300 cm^{-1} ; C, 1700 cm^{-1} ; CNH, 1550 cm^{-1} ; NHCS, 1360 cm^{-1}. In the i.r. spectra of all the compounds listed in Table the peaks for the above functional groups appear nearly at 2940 and 3250 cm^{-1} ; 1700 cm^{-1} ; 1540 cm^{-1}, respectively. Semicarbazides gives sharp peak at about 1640 for -C(=O)-NH. Twelve thiosemicarbazides have been evaluated for their antiacetyl cholinesterase activity, however six compounds showed inhibition.

Experimental

Melting points were taken in open capillary tubes and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. N-aryl piperazines(I) (R=H, 3-CH_3 & 4-CH_3) were prepared according to known procedures[10,11].

1-piperazine acetic acid 4-aryl ethyl ester (II, Table I)

The equimolar quantities of 1-aryl piperazine (0.01 m), K_2CO_3 (0.01 m) (anhydrous) and chloroethylacetate (0.01 m) were taken in 20 ml dry benzene and mixture was refluxed for 8-16 hrs. The reaction time in each case was determined by TLC on silica



gel G. The ester showed R_f values higher than the 1-aryl piperazines. The hot mixture was evaporated and the residue was washed with water and then extracted with benzene, benzene layer was separated and dried over anhydrous $MgSO_4$. Now it is concentrated and distilled under reduced pressure.

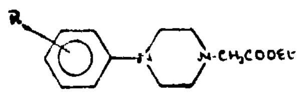
1-piperazine acetic acid-4-aryl-hydrazides (*III*, *Table 2*)

To a solution of .01 mole of ester (II) in 5 ml ethyl alcohol (absolute) was added 0.015 mole of hydrazine hydrate. The mixture was refluxed for 6-12 hrs and reaction time was determined by TLC. The ester showed R_f value higher than the hydrazides. Ethyl alcohol was evaporated and residue was distilled or crystallised as the case may be.

N'-[(N-aryl-N'-acetyl) piperazine]-N⁴-methyl/phenyl Semicarbazide or aryl thiosemicarbazide : (*IV*, *Table 3*)

A mixture of 0.01 mole of 1-piperazine acetic acid-4-arylhydrazide(III) and 0.01 mole of appropriate isocyanate or isothiocyanate in 30 ml of dry benzene was refluxed on steambath for 4 hours. The reaction mixture cooled and solid mass which separated out was filtered and crystallised from suitable

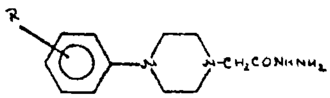
TABLE 1



S. No.	R.	M. P. °C/Press or B. P. m.m.	Yield %	Molecular formulae	Analysis % C H N Calc.	Found
1.	H[a]	135-140/3	60	$C_{14}H_{20}N_2O_2$	C 67.74 H 8.06 N 11.29	67.35 8.00 11.00
2.	2-CH_3	155-160/3	50	$C_{15}H_{22}N_2O_2$	C 68.71 H 8.39 N 10.80	68.25 8.10 10.50
3.	3-CH_3	160-65/3	50	$C_{15}H_{22}N_2O_2$	C 68.71 H 8.39 N 10.80	69.00 8.20 10.20
4.	4-CH_3[b]	57	60	$C_{15}H_{22}N_2O_2$	C 68.71 H 8.39 N 10.80	68.30 8.30 10.40

a. Lit[1a] B. P. 194°C/8 m. m.
b. recrystallised from C_6H_6/Petroleum ether

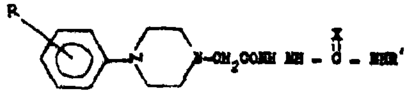
TABLE 2



S. No.	R	M. P. °C	Yield %	Molecular Farmulae	Analysis % C H N Calc.	Found
1.	H	75	55	$C_{12}H_{18}N_4O$	C 61.55 H 7.69 N 23.93	61.10 7.20 23.60
2.	2-CH_3	nil	50	$C_{13}H_{20}N_4O$	C 62.71 H 8.06 N 22.57	62.25 8.00 22.15
3.	3-CH_3	60	60	$C_{13}H_{20}N_4O$	C 62.71 H 8.06 N 22.57	62.32 8.15 22.35
4.	4-CH_3	130	65	$C_{13}H_{20}N_4O$	C 62.71 H 8.06 N 22.57	63.00 8.35 22.15

Recrystallising solvent C_6H_6/Petroleum ether

TABLE—3



S. No.	R	R′	X	M.P.°C	Recrystallising solvent	Molecular Formulae		Analysis % Calculated	Found
1.	H	Phenyl	S	197	ethanol	$C_{19}H_{23}N_5OS$	C	61.79	62.00
							H	6.23	6.40
							N	18.92	18.50
2.	H	2-Methyl phenyl	S	163	do	$C_{20}H_{25}N_5OS$	C	62.66	62.50
							H	6.52	6.00
							N	17.86	18.00
3.	H	3-Methyl phenyl	S	180	do	$C_{20}H_{25}N_5OS$	C	62.66	62.76
							H	6.52	6.50
							N	17.86	17.93
4.	H	4-Methyl phenyl	S	168	do	$C_{20}H_{25}N_5OS$	C	62.66	63.00
							H	6.52	7.00
							N	17.86	17.40
5.	H	4-Cl-Phenyl	S	194	do	$C_{20}H_{24}ClN_5OS$	C	57.41	57.00
							H	5.74	5.76
							N	16.74	17.00
6.	H	4-Br-Phenyl	S	192	do	$C_{20}H_{24}BrN_5OS$	C	51.95	52.00
							H	5.19	5.20
							N	15.14	15.60
7.	3-CH_3	Phenyl	S	162	do	$C_{20}H_{25}N_5OS$	C	62.66	63.05
							H	6.52	6.42
							N	17.86	17.96
8.	3-CH_3	2-Methyl phenyl	S	155	do	$C_{21}H_{27}N_5OS$	C	63.47	63.86
							H	6.88	6.56
							N	17.63	17.40
9.	3-CH_3	3-Methyl phenyl	S	170	do	$C_{21}H_{27}N_5OS$	C	63.47	63.96
							H	6.88	6.80
							N	17.63	18.00
10.	3-CH_3	4-Methyl phenyl	S	172	DMF & ethanol	$C_{21}H_{27}N_5OS$	C	63.47	63.76
							H	6.88	6.38
							N	17.63	17.21
11.	3-CH_3	4-Cl-phenyl	S	196	ethanol	$C_{21}H_{26}ClN_5OS$	C	58.48	58.00
							H	6.03	5.86
							N	16.23	15.89
12.	3-CH_3	4-Br-Phenyl	S	187	DMF & ethanol	$C_{21}H_{26}BrN_5OS$	C	52.94	53.00
							H	5.50	5.14
							N	14.70	14.50
13.	4-CH_3	Phenyl	S	186	ethanol	$C_{20}H_{25}N_5OS$	C	62.66	62.18
							H	6.52	6.12
							N	17.86	17.80
14.	4-CH_3	2-Methyl phenyl	S	172	do	$C_{21}H_{27}N_5OS$	C	63.47	63.50
							H	6.88	6.48
							N	17.63	18.06
15.	4-CH_3	3-Methyl phenyl	S	196	do	$C_{21}H_{27}N_5OS$	C	63.47	63.00
							H	6.88	6.42
							N	17.63	18.00
16.	4-CH_3	4-Methyl phenyl	S	190	do	$C_{21}H_{27}N_5OS$	C	63.47	63.15
							H	6.88	7.00
							N	17.63	18.20
17.	4-CH_3	4-Cl-Phenyl	S	200	DMF & ethanol	$C_{21}H_{26}ClN_5OS$	C	58.48	58.60
							H	6.03	6.25
							N	16.23	16.46
18.	4-CH_3	4-Br-Phenyl	S	188	do	$C_{21}H_{26}BrN_5OS$	C	52.94	52.84
							H	5.50	5.42
							N	14.70	14.84
19.	H	Methyl	O	199	ethanol	$C_{14}H_{21}N_5O_2$	C	57.62	57.16
							H	7.21	7.11
							N	24.05	23.63
20.	H	Phenyl	O	146	do	$C_{19}H_{23}N_5O_2$	C	64.58	65.10
							H	6.51	6.48
							N	19.82	20.15

TABLE—3 (Contd.)

21.	3-CH_3	Methyl	O	195	do	$C_{16}H_{23}N_5O_2$	C H N	59.02 7.54 22.95	58.81 8.06 23.15
22.	3-CH_3	Phenyl	O	155	do	$C_{21}H_{25}N_5O_2$	C H N	66.50 9.60 18.47	66.56 6.36 18.54
23.	4-CH_3	Methyl	O	215	do	$C_{16}H_{23}N_5O_2$	C H N	59.02 7.54 22.95	59.00 7.06 22.45
24.	4-CH_3	Phenyl	O	181	Benzene	$C_{21}H_{25}N_5O_2$	C H N	66.50 6.60 18.47	66.12 6.60 18.23

solvent. Physical constants of the compounds thus prepared are listed in the Table.

Biological Data :

Enzyme preparation : Male adult albino rats weighing approximately 200-220 gm. were killed by decapitation. Brains were quickly removed and homogenized in ice-cold 0.25 *M* sucrose with the help of a Potter-Elvehjem type homogenizer fitted with a teflon pestle.

Determination of acetyl cholinesterase (AChE) activity

The method of Hestrin[13] as described by Colwick and Kalpan[14] was used. The reaction mixture in a final volume of 1.5 ml contained 0.075 *M* phosphate bnffer, *p*H 7.4, 4 *M* acetylcholine and 0.2 ml of 10% (w/v) homogenate. The reaction mixture with or without test compounds was incubated in a constant temperature water bath for 5 minutes after which the reaction was started with the addition of acetylcholine. The reaction was stopped after 10 mins. with the addition of 2 ml of alkaline hydroxylamine reagent (made by mixing equal volumes of 3.5 *N* NaOH and 2*M* hycroxylamine within an hour of use). Immediately after the addition of hydroxylamine reagent, 1 ml of cold 4*N* HCl was added to precipitate the protein as well as to bring the *p*H sufficiently acidic (*p*H 1 to 2). After centrifugation (at 500×g for 5 min) the supernatant was transferred into a separate tube. Colour was developed promptly by adding 1 ml of 0.37 *M* ferric chloride in 0.1*N* HCl and intensity of colour was measured at 540 *M*. All compounds were dissolved in propylene glycol (100%) and used at 3×10^{-4} *M*. A control containing equal volume of propylene glycol was also run in parallel. Each assay was done in duplicate.

Results

Compounds from serial number 1 to 18 of Table 3 were tested and six compounds namely 3, 6, 7, 9, 12 and 14 showed marginal inhibition.

Acknowledgement

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Studies in Benzofurans. Part IV : Synthesis of some 2-Substituted and 2, 3-Pisubstituted 3, 4-Dihydro-4-Oxobenzofuro [3, 2-d] Pyrimidines

S. B. MAHAJAN* AND Y. S. AGASIMUNDIN**

Department of Chemistry, Karnatak University Post Graduate Centre, Gulbarga-5

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Synthesis of some 3-acylaminobenzofuran-2-carboxylic acids and their transformation into 2-substituted-3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidines through 2-substituted-4-H-benzofuro [3, 2-d]-m-oxazin-4-ones and into 2, 3-disubstituted 3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidines by the action of aromatic amines in the presence of phosphorus trichloride is described.

THE importance and the need for the study of benzofuro [3, 2-d] pyrimidine derivatives has been stressed in our earlier publication[1] and it has been shown that such compounds may conveniently be obtained by constructing pyrimidine ring on suitable benzofuran derivatives. Niementowski reaction has been widely employed for the synthesis of fused pyrimidine systems[2]. Now in an effort to extend this reaction for the synthesis of benzofuro [3, 2-d] pyrimidines, attempts were made to get the required 3-aminobenzofuran-2-carboxylic acid by the hydrolysis of the easily accessible ester (I). Although it could be hydrolysed readily, the acid could not be isolated due to its decarboxylation soon after precipitation. However the hydrolysis of I in alcoholic potash gave the potassium salt of the desired acid in an highly crystalline form. The treatment of this salt with acetic anhydride gave a product which is identified as 2-methyl-4-H-benzofuro [3, 2-d]-m-oxazin-4-one (XIII) on the basis of IR data and elemental analysis. Infrared spectrum shows a strong band at 1780 cm^{-1} characteristic of C=O of such oxazinones[3]. This is further confirmed by its synthesis through an unambiguous method. Thus I on acetylation and hydrolysis gave 3-acetamidobenzofuran-2-carboxylic acid (VII) which on cyclodehydration in acetic anhydride gave an identical product. Treatment of oxazinone (XIII) with ammonia followed by dilute aqueous alkali gave a product which is identified as 2-methyl-3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidine (XVII) by comparison with an authentic sample[4].

Similar cyclodehydration of 3-propionamido, 3-benzamido and 3-phenylacetamidobenzofuran-2-carboxylic acids obtatined by the acylation and hydrolysis of I gave the corresponding 2-substituted oxazinones (XIV-XVI) in excellent yields. Infrared spectra of all these compounds exhibit the characteristic absorption at 1750-1780 cm^{-1} region. 2-Ethyl and 2-benzyl-oxazinones (XIV and XVI) reacted readily with ammonia and aqueous alkali to give 2-ethyl and 2-benzylbenzofuropyrimidinones (XVIII and XIX), but 2-phenyloxazinone failed to undergo a similar reaction under a variety of conditions. Identical products (XVIII and XIX) were obtained by the cyclisation of respective 3-acylamino-benzofuran-2-carboxamides (XI and XII) in presence of dilute aqueous alkali. Both XVIII and XIX exhibit characteristic IR absorptions at 1690 and 3090 cm^{-1} due to C=O and NH respectively of pyrimidinones.

Fused 2, 3-disubstituted 3, 4-dihydro-4-oxopyrimidine systems are best prepared from O-acylamino-carboxylic acids in a single step[5]. Now as a typical example VII is subjected to such a reaction with a few aromatic amines in presence of phosphorus trichloride and the corresponding 2, 3-disubstituted 3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidines (XX-XXVI) were obtained in good yields. The presence of absorption bands at 1680 and 1610-1615 cm^{-1} due to C=O and C=N groups respectively and the absence of any peak in the 3100 cm^{-1} region due to NH group is in agreement with these structures.

All the 3-acylaminobenzofuran-2-carboxylic acids (VII-X) were decarboxylated to the corresponding 3-acylaminobenzofurans (XXVII-XXX) just by heating above their melting points for a few minutes. Further reactions are in progress and will be reported elsewhere.

Experimental

2-Methyl-4-H-benzofuro [3,2-d]-m-oxazin-4-one (XIII) :

To a solution of potassium hydroxide (1.4 g) in

*Department of Chemistry, S. B. College of Science, Gulbarga.
**To whom all the correspondance should be addressed.



I R=H; R'=OEt

II R=H; R'=NH_2

III R=$COCH_3$; R'=OEt

IV R=COC_2H_5; R'=OEt

V R=COC_6H_5; R'=OEt

VI R=$COCH_2C_6H_5$; R'=OEt

VII R=$COCH_3$; R'=OH

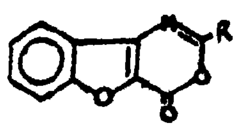
VIII R=COC_2H_5; R'=OH

IX R=COC_6H_5; R'=OH

X R=$COCH_2C_6H_5$; R'=OH

XI R=COC_2H_5; R'=NH_2

XII R=$COCH_2C_6H_5$; R'=NH_2

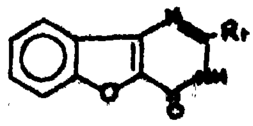


XIII R=CH_3

XIV R=C_2H_5

XV R=C_6H_5

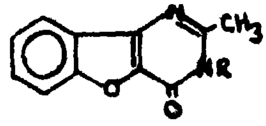
XVI R=$CH_2C_6H_5$



XVII R=CH_3

XVIII R=C_2H_5

XIX R=$CH_2C_6H_5$



XX R=C_6H_5

XXI R=C_6H_4Cl (p)

XXII R=C_6H_4Br (p)

XXIII R=$C_6H_4CH_3$ (p)

XXIV R=$C_6H_4OCH_3$ (p)

XXV R=$C_6H_4OC_2H_5$ (p)

XXVI R=$C_{10}H_7$ (p)



XXVII R=CH_3

XXVIII R=C_2H_5

XXIX R=C_6H_5

XXX R=$CH_2C_6H_5$

absolute ethanol (45 ml), ethyl-3-aminobenzofuran-2-carboxylate (1. 2g) was added and the reaction mixture was heated under reflux for about 45 minutes on a water bath. The colourless crystalline potassium salt of 3-amino-benzofuran-2-carboxylic acid starts separating while refluxing. After cooling, the salt was collected by filtration.

The dry salt (1. g) was heated under reflux in acetic anhydride (8 ml) for about 1 hour. The reaction product was poured on ice with stirring. The solid thus separated was collected and crystallised from ethanol as colourless needles (0.75 g), m.p. 151° (Found : C, 65. 54 ; H, 3.61 ; N, 6.85, $C_{11}H_{7.5}O_3N$ requires C, 65.67, H, 3.48, N, 6.97%).

Ethyl-3-acetamidobenzofuran-2-carboxylate (III)

I (1 g) was treated with acetic anhydride (4 ml) and then warmed on water bath for 30 minutes. The reaction product on decomposition with ice water gave a colourless solid.

Similarly ethyl-3-propionamidobenzofuran-2-carboxylate (IV) was prepared by using propionic anhydride. Details are reported in Table 1.

Ethyl-3-benzamidobenzofuran-2-carboxylate (V) :

I (5 g.) was suspended in 2 N aqueous sodium hydroxide (50 ml) and then treated with benzoyl chloride (15 ml) in portions while vigorously shaking. After shaking for 30 minutes the reaction product was filtered, washed with water and crystallised from suitable solvent.

Similarly ethyl-3-phenylacetamidobenzofuran-2-carboxylate (VI) was prepared by using phenylacetyl chloride. Details are reported in Table 1.

General method for the preparation of 3-acylaminobenzo furan-2-carboxylic acids (VII-X) :

Ethyl-3-acylaminobenzofuran-2-carboxylate (5 g) was dissolved in suitable volume of ethanol by warming and then treated with a solution of ethanolic potash (2.5 g in 25 ml of ethanol). The reaction mixture was just boiled for 2 minutes, diluted with water and cooled in ice. Acidification with dilute hydrochloric acid liberated the carboxylic acid as colourless solid, which was then filtered, washed with water and crystallised from suitable solvent.

The acids thus prepared are recorded in Table 1.

TABLE—1

Compound	M.P. °C	S	Yield %	Mol. Formula	Analysis % Required C	H	N	Found C	H	N
III	166	a	92	$C_{13}H_{13}O_4N$	63.16	5.26	5.67	63.45	5.51	5.97
IV	142	a	80	$C_{14}H_{15}O_4N$	64.37	5.75	5.36	64.61	5.82	5.57
V	126	a	93	$C_{18}H_{15}O_4N$	69.90	4.85	4.53	70.15	4.53	4.77
VI	157	a	98	$C_{19}H_{17}O_4N$	70.58	5.26	4.33	70.91	5.43	4.71
VII	211(d)	a	85	$C_{11}H_9O_4N$	60.29	4.11	6.39	60.55	4.35	6.68
VIII	205(d)	c	90	$C_{12}H_{11}O_4N$	61.80	4.72	6.01	62.05	4.91	6.33
IX	200(d)	a	75	$C_{16}H_{11}O_4N$	68.32	3.91	4.98	68.59	4.08	5.21
X	207(d)	b	69	$C_{17}H_{13}O_4N$	69.15	4.41	4.75	69.35	4.61	4.96
XIII	151	c	72	$C_{11}H_7O_3N$	65.97	3.48	6.97	65.91	3.52	7.25
XIV	143	c	76	$C_{12}H_9O_3N$	66.99	4.19	6.51	67.32	4.47	6.73
XV	215	c	76	$C_{16}H_9O_3N$	73.00	3.42	5.32	73.29	3.58	5.61
XVI	151	c	72	$C_{17}H_{11}O_3N$	73.64	3.97	5.05	73.68	4.11	5.42
XVII	317	d	66	$C_{11}H_8O_2N_2$	66.01	4.00	14.01	66.17	4.15	14.34
XVIII	319	d	65	$C_{12}H_{10}O_2N_2$	67.30	4.67	13.08	67.55	4.72	13.29
XIX	283	d	60	$C_{17}H_{12}O_2N_2$	73.91	4.35	10.15	74.07	4.44	10.21
XX	235	b	58	$C_{17}H_{12}O_2N_2$	73.91	4.35	10.15	74.12	4.39	10.27
XXI	209	b	97	$C_{17}H_{11}O_2N_2Cl$	65.69	3.54	9.02	65.91	3.66	9.43
XXII	208	c	66	$C_{17}H_{11}O_2N_2Br$	57.46	3.10	7.89	57.64	3.31	8.02
XXIII	253	b	69	$C_{19}H_{14}O_2N_2$	74.49	4.83	9.66	74.57	5.01	9.87
XXIV	194	b	63	$C_{18}H_{14}O_3N_2$	70.60	4.58	9.15	70.81	4.73	9.37
XXV	209	c	60	$C_{19}H_{16}O_3N_2$	71.25	5.00	8.76	71.40	5.12	8.91
XXVI	197	c	50	$C_{21}H_{14}O_2N_2$	77.31	4.29	8.59	77.50	4.41	8.77
XXVII	169	a	80	$C_{10}H_9O_2N$	68.58	5.14	8.00	68.73	5.20	8.35
XXVIII	156	a	75	$C_{11}H_{11}O_2N$	69.84	5.82	7.41	70.11	5.97	7.91
XXIX	130	c	70	$C_{15}H_{11}O_2N$	75.97	4.64	5.91	76.19	4.81	6.30
XXX	140	a	72	$C_{16}H_{13}O_2N$	76.49	5.18	5.58	76.55	5.29	5.61

S = Solvent of crystallisation ; a = aqueous ethanol ; b = ethanol ; c = benzene-petroleum ether ; d = aqueous DMF.

General method for the preparation of 2-substituted 4-H-benzofuro [3, 2-d]-m-oxazin-4-ones (XIII-XVI) :

3-Acylaminobenzofuran-2-carboxylic acid (2 g) was heated under reflux in acetic anhydride (8 ml) for about 1 hour. Excess of acetic anhydride was distilled off under reduced pressure. The residual product was treated with petroleum ether and the crystalline solid thus obtained was collected and crystallised from suitable solvent. Mixed m.p. of 2-methyl-4-H-benzofuro-[3, 2-d]-*m*-oxazin-4-one with the sample obtained by the earlier method was not depressed.

Melting point, yield, analytical data etc. of the compounds thus prepared are summarised in Table 1.

General method for the preparation of 2-substituted 3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidines (XVII-XIX):

Benzofuro-oxazinone (1 g) was suspended in liquor ammonia (10 ml) and refluxed on water bath for about 1 hour. A solution of 10% aqueous sodium hydroxide (5 ml) was then added and refluxed for further 10 minutes. The reaction product was filtered and the clear filtrate when acidified with acetic acid gave the corresponding 2-substituted 3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidine as colourless solid. Solvent of crystallisation, m.p. yield, analytical results etc. of the compounds thus prepared are summerised in Table 1.

3-Propionamidobenzofuran-2-carboxamide (XI) :

II (2 g) was treated with propionic anhydride (8 ml) and warmed till a clear solution was obtained. The reaction product on decomposition with ice gave XI, which an crystallisation from aqueous ethanol was obtained as colourless needles, (2.2 g), m.p. 169° (Found : C, 62. 38 ; H, 5. 44 ; N, 12.38, $C_{12}H_{12}O_3N_2$ requires C, 62.07 ; H, 5.17 ; N, 12.07%).

3-Phenylacetamidobenzofuran-2-carboxamide (XII) :

II (2 g) was suspended in 2N aqueous sodium hydroxide (20 ml) and treated with phenylacetyl chloride (4 ml). The reaction mixture was shaken vigorously, for 30 minutes, cooled and filtered. On crystallisation from aqueous ethanol it was obtained as colourless needles, (2.6 g.), m.p. 189° (Found : C, 69.61 ; H, 4.83 ; N, 9.78, $C_{17}H_{14}O_3N_2$ requires C, 69.39 ; H, 4.76 ; N, 9.53%).

2-Ethyl-3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidine (XVIII) :

XI (12 g) was suspended in 2 N aqueous sodium hydroxide (600 ml) and warmed till a clear solution was obtained. The alkaline solution on acidification with dilute hydrochloric acid gave XVIII, as a solid, which an crystallisation from aqueous DMF was obtained as colourless needles, (9 g) m.p. 319°. Mixed m.p. with the sample obtained above was not depressed (Found : C, 67.55 ; H. 4.83 ; N, 13.41, $C_{12}H_{10}O_2N_2$ requires C, 67.30 ; H, 4.67 ; N, 13.08%).

2-Benzyl-3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidine (XIX) :

XII (12 g) was treated with 2N aqueous sodium hydroxide (600 ml) until a clear solution was obtained subsequent working up as above gave, XIX as colourless solid (6.5 g). It was crystallised from aqueous DMF as colourless needles, m.p. 283°. Mixed m.p. with the sample obtained by the above method was not depressed (Found ; C, 74.15 ; H, 4.51 ; N, 10.38, $C_{17}H_{12}O_2N_2$ requires C, 73.91 ; H, 4.35 ; N, 10.15%).

General Procedure for the synthesis of 2-methyl-3-aryl-3, 4-dihydro-4-oxobenzofuro [3, 2-d] pyrimidines (XX-XXVI) :

3-Acetamidobenzofuran-2-carboxylic acid (VII, 0.01 mole) and aromatic amine (0.01 mole) were dissolved in dry toluene (25 ml) and a solution of phosphorus trichloride (0.6 ml) in dry toluene (5 ml) was added in portions with vigorous shaking. After the addition is over the reaction mixture was heated under reflux in an oil bath at 130° for 2 to 4 hours. The reaction product, after cooling was treated with 10% aqueous sodium carbonate (25 ml) and then subjected to steam distillation to remove toluene. The crystalline solid thus separated was collected and crystallised from suitable solvent. Crystallisation solvent, m.p. yield, analytical data etc. are recorded in Table 1.

3-Acylaminobenzofurans (XXVII-XXX) :

3-Acylaminobenzofuran-2-carboxylic acid (1 g) was heated above its melting point for about 40 minutes. The product was washed with aqueous sodium bicarbonate and the insoluble material so obtained was crystallised from suitable solvent. Compounds thus prepared are described in Table 1.

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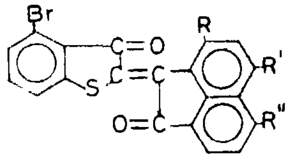
Studies on Thioindigoid Dyes

K. D. BANERJI, A. K. D. MAZUMDAR AND S. K. GUHA
Department of Chemistry, Bhagalpur University, Bhagalpur-812007

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Preparation and properties of three classes of dyes obtained by the condensation of 4-bromo-3-hydroxythionaphthene with acenaphthenequinones, phenanthraquinones and benzaldehydes have been reported. The λ_{max} values have been noted and reasons for the variation of colour in the dyes have been offered.

IN this communication we report the preparation and properties of the dyes shown in structures I a-d, II a-c and III a-c which have been obtained by the condensation of 4-bromo-3-hydroxythionaphthene[1] with the appropriate acenaphthenequinones, phenanthraquinones and benzaldehydes.

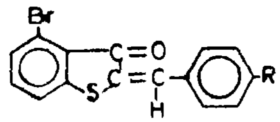


	R	R′	R″
Ia	H	H	H
Ib	OCH_3	H	H
Ic	H	Cl	H
Id	H	NO_2	NO_2

The acenaphthylene indigos (I a-d) possess intense violet-brown, chocolate-brown or brownish red colour. The dyes offered great resistance to reduction by hydrosulphite and formed the greenish yellow vats. The shades on cotton could not be fully developed. Details about the dyes are given in Table.

A comparison of the λ_{max} values of the dyes Ia and Ib with similar dyes having the bromine atom[2-4] in positions 5-, 6-, and 7-, respectively, reveals that on this basis the depth of colour of the dyes could be arranged as under : 5-bromo dye >4-bromo dye >7-bromo dye >6-bromo dye.

It will, however, be noticed from the absorption data (Table) that while a methoxy substituent at position 1′ (of the acenaphthene moiety) has a bathochromic effect, a chlorine atom at 3′ or two or nitro groups at 3′ and 4′, cause the opposite effect. The reasons for these apparently anamolous results are not obvious from the usual electronic considerations and the explanations are without doubt more involved.



	R
IIa	H
IIb	$N(CH_3)_2$
IIc	NO_2

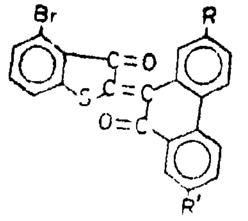
TABLE 1

Dye	Name of Reactants	Name of dye	Appearance Yield %	Solvent of crystallisation M.P.C.	λ_{max} in mμ
Ia	T+AQ	2-(4-Bromo)-thionaphthene-AI	Violet brown 78	Pyridine 269-270	527
Ib	T+Methoxy-AQ	2-(4-Bromo)-thionaphthene-8′-(1-methoxy) AI	Violet brown 78	Pyridine 292-293	520
Ic	T+3-Chloro-AQ	2-(4-Bromo)-thionaphthene-8′-(3-chloro)-AI	Brownish red 72	Pyridine 337-338	515
Id	T+3 : 4-Dinitro-AQ	2-(4-Bromo)-thionaphthen-8′ (2′-4′-dinitro)-AI	Chocolate 74	Pyridine 299-300	510
IIa	T+Benzaldehyde	B-2(4-Bromo) 3-oxy 2,3 dihydro thionaphthene	Intense Yellow 82	Ethanol 137-138	440
IIb	T+N,N-Dimethylamino-benzaldehyde	4′-Dimethylamino-B-2-(4-Bromo) 3-oxy 2,3 dihydrothionaphthene	Violet 84	Acetic acid 195-196	490
IIc	T+4-Nitrobenzaldehyde	4′-Nitro-B-2-(4-Bromo) 3-oxy 2,3 dyhydro thionaphthene	Orange 80	Acetic acid 207-208	442
IIIa	T+PQ	2-(4-Bromo)-thionaphthene-9′-PI	Black 68	Pyridine 300-302	554
IIIb	T+2-Nitro-PQ	2-(4-Bromo)-thionaphthene-9′-(2′-nitro)-PI	Deep chocolate 72	Pyridine 325(d)	540
IIIc	T+2:7-Dinitro-PQ	2-(4-Bromo)-thionaphthene-9′-(2′-7′-dinitro)-PI	Brownish black 78	Pyridine 360	545

T=4-Bromo3-hydroxythionaphthene, AQ=Acenaphthene quinone, AI=Acenaphthyleneindigo, B=benzylidene, PQ=Phenanthraquinone, PI=Phenanthrene indigo.

The shades of the benzylidene dyes IIa-c reported herein vary from violet to orange to intense yellow. They are all soluble in methanol, ethanol, acetic acid, xylene, pyridine etc., δ Attempts to reduce these dyes by hydrosulphite were not quite successful and even moderate shades could not be developed on cotton. The λ_{max} values of the dyes (*vide* Table) when compared with similar dyes with the position of the bromine atom in thionaphthene substrate varying [2-4] from 5 to 6 to 7, now enable us to conclude that the depth of colour varies in these series also as follows :

5-bromo dye >4-bromo dye >7-bromo dye >6-bromo dye.



	R	R'
IIIa	H	H
IIIb	NO_2	H
IIIc	NO_2	NO_2

The phenanthrene indigos IIIa-c all have intense colour (black, deep-chocolate, and brown-black) but these dyes again could not be uniformly developed on cotton from the hydrosulphite vats, These dyes, however, absorb maximaly at appreciably higher wavelength than those discussed in the previous paragraphs, apparently because the three aromatic π sextets of the phenanthrene system extend the area of the electron cloud and thus lead to enhanced absoption maxima. A nitro group at position 2 causes a hypsochromic effect, compared to the unsubstituted dye, due obviously to electron withdrawl from the phenanthren ring system. The two nitro groups at 2 and 7, however, cause a slightly lesser hypsochromic effect, than a single nitro group at 2 probably because these two nitro groups somewhat neutralise one another's effect on the main chromophore system. However, when the λ_{max} values of the dyes obtained by condensation of 4-bromo-, 5-bromo-, 6-bromo-, and 7-bromo-3-hydroxythionaphthene individually with phenanthraquinone and its mono and dinitro deriatives respectively,[2-4] are compared, here too we get the order of depth of colour as

5-bromo dye > 4-bromo dye > 7-bromo dye > 6-bromo dye > parent dye.

Acenaphthyleneindigos (I a-d) :

Molar quantities of the reactants were dissolved in minimum volumes of hot glacial acetic acid, which were then mixed and refluxed for 20-30 minutes with the addition of conc. HCl (8 ml). The crude products were filtered, washed and crystallised from pyridine.

Phenanthreneindigos (III a-c) :

These dyes were similarly prepared from the constituents in glacial acetic acid solution and heating for 30 minutes with the addition of conc. HCl (10 ml). The crude dyes were filtered, washed and crystallised from pyridine.

Thioindogenides (II a-c) :

These dyes were obtained from equimolecular quantities of the reactants in boiling absolute ethanolic solution (20 ml), adding conc. HCl (2 ml) and heating under reflux for 15 minutes. The crude dyes were filtered, washed and crystallised from suitable solvents several times to get the pure products.

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Studies on 4, 4'-Dihydroxydiphenyl Sulfone and 4, 4'-Dihydroxydiphenyl Ether

S. P. PRAJAPATI, J. H. PARDANANI AND SURESH SETHNA

Chemistry Department, Faculty of Science, M. S. University of Borada, Baroda-2

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The synthesis of bi(6-flavonyl)sulfone and bi(2- and 3-methyl-5-benzofuranyl) sulfone from 4 4'-dihydroxy diphenyl sulfone and that of bi (6-chromonyl) ether and its 2-methyl and 2-methyl-3-acetyl derivatives, bi(6-flavonyl) ether and bi(3-methyl-5-benzofuranyl) ether from 4, 4'-dihydroxy diphenyl ether have been described.

IN continuation of our previous work on 4,4'-dihydroxydiphenyl methane[1] we have now synthesised some oxygen heterocycles from 4,4'-dihydroxydiphenyl sulfone[2] and 4-4'-dihydroxydiphenyl ether.

For the synthesis of bi(6-flavonyl)sulfone (Ia) the required intermediate 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfone was obtained though the Fries migration of 4,4'-diacetoxydiphenyl sulfone. The structure was established by preparing the same compound by the oxidation of 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfide with hydrogen peroxide according to Kulkarni[3]. This was further confirmed by the oxidation of the dimethyl ether of the diacetyl sulfone with alkaline potassium permanganate to the known 4,4'-dimethoxydiphenyl sulfone-3,3'-dicarboxylic acid[4].

3,3'-Diacetyl-4,4'-dihydroxydiphenyl sulfone was condensed with benzaldehyde in the presence of alcoholic potassium hydroxide. The bichalconyl derivative so obtained on cyclisation and dehydrogenation with selenium dioxide gave bi(6-flavonyl) uslfone.

The synthesis of bi(3-methyl-5-benzofuranyl) sulfone (IIa) has been achieved by condensing 3,3'-diacetyl-4,4'-dihydroxydiphenyl sulfone with ethyl bromoacetate. The 3,3'-diacetyl-4,4'-di(carbethoxymethoxy) diphenyl sulfone obtained was hydrolysed to the corresponding dicarboxylic acid. This was then heated with sodium acetate and acetic anhydride when through simultaneous cyclisation and decarboxylation the desired benzofuran derivative was obtained. For the synthesis of bi(2-methyl-5-benzofuranyl) sulfone (IIb), 4,4'-dihydroxydiphenyl sulfone was converted into its diallyloxy derivative and this was converted into 3,3'-diallyl-4,4'-dihydroxydiphenyl sulfone by heating with diphenyl ether. The allyl phenol was converted into its acetoxy derivative and then brominated. The tetrabromo derivative was subjected to the action of potassium hydroxide in alcohol according to Kaufman *et al*[5] when the desired benzofuran derivative was obtained.

Attempt to prepare 3,3'-diformyl-4,4'-dihydroxy diphenyl sulfone by direct formylation of 4,4'-dihydroxydiphenyl sulfone with hexamine or with dimethyl formamide did not succeed.

Some oxygen heterocycles have also been synthesised from 4,4'-dihydroxydiphenyl ether. The intermediate 3,3'-diacetyl-4,4'-dihydroxydiphenyl ether required was obtained through the Fries migration of 4,4'-diacetoxy diphenyl ether. On condensation with ethyl acetate in the presence of pulverised sodium, it gave directly bi(2-methyl-6-chromonyl) ether (Ib). The Kostanecki-Robinson acetylation of the same ketone gave bi(2-methyl-3-acetyl-6-chromonyl) ether (Ic). The synthesis of bi(6-chromonyl) ether was achieved through cyanoethylation of 4,4'-dihydroxy diphenyl ether with acrylonitrile. 4,4'-Dicyanoethoxy diphenyl ether obtained, on hydrolysis gave the corresponding acid, which was cyclised with polyphosphoric acid to bi(6-chromanonyl) ether which on dehydrogenation with palladised charcoal resulted in bi(6-chromonyl) ether (Id).

The condensation of 4,4'-dihydroxy diphenyl ether with either malic acid in the presence of sulphuric acid or with ethyl acetoacetate in the presence of different condensing agents like conc. sulphuric acid, anhydrous aluminium chloride in nitrobenzene at 130° and in boiling diphenyl ether did not succeed.

3,3'-Diacetyl-4,4'-dihydroxy diphenyl ether was condensed with diethyl carbonate in the presence of pulverised sodium to get bi(4-hydroxy-6-coumarinyl) ether.

The synthesis of bi(3-methyl-5-benzofuranyl) (IIc) has been achieved by condensing 3,3'-diacetyl-4-4'-dihydroxy diphenyl ether with ethyl bromoace-

tate, hydrolysis of the diester obtained to the corresponding dicarboxylic acid and heating with sodium acetate and acetic anhydride when simultaneous cyclisation and decarboxylation gave the desired benzofuran derivative.

Biflavonyl ethers such as hinokiflavone[6] are found to occur in nature and it was therefore thought of interest to synthesize bi(6-flavonyl) ether from 3,3'-diacetyl-4,4'-dihydroxydiphenyl ether as an illustration of a new approach towards the synthesis of such compounds. This was converted into its dibenzoyloxy derivative by reacting it with benzoyl chloride. This rearranged to 3,3'-di(benzoyl-acetyl)-4-4'-dihydroxy diphenyl ether with pyridine and powdered potassium hydroxide. The cyclisation of the diketone with conc. sulphuric acid gave bi(6-flavonyl)ether (Ie).

Attempt to formylate 4,4'-dihydroxy diphenyl ether with hexamine with a view to obtain the 3,3'-diformyl derivative required for the synthesis of other oxygen heterocycles did not succeed.

Experimental

3,3'-Diacetyl-4,4'-dihydroxydiphenyl sulfone : A mixture of 4,4'-diacetoxydiphenyl sulfone (1 g) and anhydrous aluminium chloride (2 g.) was heated in an oil bath at 150-60° for 5 hrs. and the product obtained on addition of ice-cold hydrochloric acid was taken up in sodium hydroxide solution. The product obtained on acidification crystallised from acetic acid in light brown needles (0.3 g.), m.p. 189-190°. It gave a red colouration with alcoholic ferric chloride (Found : C, 57.59 ; H, 4.06, $C_{16}H_{14}O_6S$ requires C, 57.50 ;H, 4.19%.)

The di(2,4-DNP) : Prepared as usual and crystallised from diphenyl ether in orange needles gave m.p. 305-06°. (Found : N, 16.00 $C_{28}H_{22}N_8O_{12}S$ requires N, 16.14%.)

The dimethyl ether : A mixture of 3,3'-diacetyl-4,4'-dihydroxy diphenyl sulfone (1 g.), dimethyl sulfate (1.5 ml.) and anhydrous potassium carbonate (3 g.) in dry acetone was refluxed for 12 hr. The solvent was removed and water added. The product obtained crystallised from alcohol in white shining plates (0.8 g.), m.p. 179°. (Found : C, 59.87 ; H, 4.89, $C_{18}H_{18}O_6S$ requires C, 59. 68 ; H, 4.97%.)

Oxidation : 4,4'-Dimethoxydiphenyl sulfone-3,3' dicarboxylic acid was obtained by refluxing the above dimethyl ether (0.5 g.) with potassium permanganate (2 g.) and potassium hydroxide solution (20 ml ; 10%) for 6 hr. It crystallised from alcohol, m.p. 252° (decomp.) Kolhatkar and Bokil[4] reported, m.p. 250° (decomp.)

Bi(6'-hydroxy-3'-chalconyl) sulfone : A mixture of 3,3'-diacetyl 4,4'-dihydroxydiphenyl sulfone (1 g) benzaldehyde (2.5 g) and potatsium hydroxide (5 g in 5 ml water) in alcohol (30 ml) was kept at room temperature for 24 hr. It was then diluted with water and acidified. The solid obtained crystallised from glacial acetic acid, m.p. 208-210°, yield 0.5 g. It gave red colour with conc. sulphuric acid and a positive Wilson test. It also showed a single spot in TLC. (Found : C, 70.53 ; H, 4.34, $C_{30}H_{22}O_6S$ requires C,70.60 ; H, 4.31%.)

Bi(6'-methoxy-3'-chalconyl) sulfone : Prepared by refluxing a mixture of the above chalcone (0.5 g), dimethyl sulfate (0.8 ml.) and anhydrous potassium carbonate (2 g.) in dry acetone for 15 hr. and crystalised from acetic acid in yellow plates (0.3 g,) gave m.p. 175-77°. (Found : C. 71.03 ; H, 4.75, $C_{32}H_{26}O_6S$ requires C, 71.36 ; H, 4.83%).

Bi(6-flavonyl) sulfone : Bi(6'-hydroxy-3' chalconyl) sulfone (0.5 g.) was refluxed with selenium dioxide (3 g.) in iso-amyl alcohol (50 ml) for 25 hr. It was then filtered hot. The filtrate was cooled and diluted with excess of petroleum ether. The separated product, crystallised from acetic acid gave m.p. 324-226°, yield 0.1 g. It gave a light blue fluorescence with conc. sulfuric acid (Found : C, 71.53 ; H, 3.40, $C_{30}H_{18}O_6S$ requires C, 71.13 ; H, 3.56%.) IR. 1645 cm^{-1} (>C=O) ; UV λ_{max} 268, 296 nm.

3,3'-Diactyl-4,4'-di(carbethoxymethoxy) diphenyl sulfone :

A mixture of 3,3'-diacetyl-4,4'-dihydroxy-diphenyl sulfone (2 g), ethyl bromoacetate (2.5 g) and anhydrous potassium carbonate (5 g) was refluxed in dry acetone for 15 hr. The product obtained on removal of acetone was washed with water and crystallised from alcohol in white needles (1g.) m.p. 139-40°. (Found : C, 57.38; H, 5.16. $C_{24}H_{26}O_{10}S$ requires C, 56,91 ; 5.1 4%.)

3,3'-Diacetyl-4,4'-di(carboxymethoxy) diphenyl sulfone :

The above ester (1 g) in glacial acetic acid (15 ml) was refluxed with conc. hydrochloric acid (15 ml) for 3 hr. The reaction mixture was poured in water and the separated product was purified by sodium bicarbonate treatment. The product obtained on acidification of the bicarbonate extract crystallised from dilute alcohol in white needles (0.5 g), m.p.222° (decomp.) (Found : C, 53.40 ; H, 3.80, $C_{20}H_{18}O_{10}S$ requires C, 53.34 ; H, 4.00%).

Bi(3-methyl-5-benzofuranyl) sulfone : Obtained from the above dicarboxylic acid (0.5 g) by refluxing with sodium acetate (2 g) and acetic anhydride (8 ml) for 1 hr. and crystallised from dilute alcohol in pale-brown needles (0.1 g) gave m.p. 152-153°. (Found : C, 66.13 ; H, 4.00, $C_{18}H_{14}O_4S$ requires C, 66.26 : H, 4.29%) IR 885 cm^{-1} (furan ring breathing) UV λ_{max} (chloroform) 248, 284 nm.

4,4'-Diallyloxydiphenyl sulfone : A mixture of 4,4'-dihydroxy diphenyl sulfone (1 g), allyl bromide (1.2 ml) and anhydrous potassium carbonte (3 g)

was refluxed in dry acetone for 8 hr. The solvent was removed and water was added. The product obtained. crystallised from alcohol in white shining plates (0.7 g), m.p. 141-42°. (Found : C, 65.61 ; H, 5.16, $C_{18}H_{18}O_4S$ requires C, 65.46 ; H, 5.46%).

3,3'-Diallyl-4,4'-dihydroxyphenyl sulfone :

The above ether (0.5 g) was refluxed in diphenyl ether (5 ml) for 2 hr. The reaction mixture was dissolved in ether and extracted with dilute sodium hydroxide solution. The product obtained on acidification of the clear alkaline extract crystallised from xylene in white needles (0.3 g), m.p. 151-52°. (Found : C, 65.31 ; H, 5.15, $C_{18}H_{18}O_4S$ requires C, 65.46 ; H, 5.46%.)

Bi(2-methyl-5-benzofuranyl) sulfone :

The above diallyl derivative (1 g) was acetylated by heating with sodium acetate (2 g) and acetic anhydride (5 ml) on a steam bath for 4 hr. The diacetoxy derivative was dissolved in chloroform and treated with bromine (1 g) in chlorform (10 ml). The product obtained on removal of chloroform was refluxed with ethanolic potassium hydroxide (1.5 g) OH in 50 ml alcohol) for 6 hr. The solvent was evaporated and the residue washed with water. The alkali insoluble product crystallised from alcohol in yellowish-brown buds (0.2 g), m.p. 154-55° (Found: C, 66.68 ; H, 4.58, $C_{18}H_{14}O_4S$ requires C, 66.26 ; H, 4.29%.) IR, 885 cm^{-1} (Furan ring breathing) UV λ_{max} (chloroform) 244, 290 nm.

4,4'-Diacetoxy diphenyl ether :

Obtained by heating 4,4'-dihydroxy diphenyl ether (3 g), acetic anhydride (15 ml) and sodium acetate (5 g) for 2 hr. and crystallised from alcohol in needles (1.3 g) gave m.p. 112°. (Found :C, 67.03 ; H, 4.83, $C_{16}H_{14}O_5$ requires C, 67.03 ; H, 4.89%).

3,3'-Diacetyl-4-4'-dihydroxy diphenyl ether :

An intimate mixture of 4,4'-diacetoxy diphenyl ether (2 g) and anhydrous aluminium chloride (5 g) was heated in an oil bath at 14° for 3 hr. The product obtained on working up as usual was crystallised from benzene, m p. 185°, yield 0 8 g. It gave a violet colour with alcoholic ferric chloride. (Found : C, 66.70 ; H, 4.66, $C_{16}H_{14}O_5$ requires C, 67.13 ; H, 4.89%).

Bi(2-methyl-6-chromonyl) ether :

A mixture of 3,3'-diacetyl-4,4'-dihydroxy diphenyl ether (15 g) ethyl acetate (15 ml) and pulverised sodium (2 g) was refluxed on a steam bath for 8 hr. The pasty mass obtained on acidification was treated repeatedly with petroleum ether and crystallised from benzene-petroleum ether-mixture. m.p. 213°. yield 0.2. g. (Found : C, 71.97 ; H, 3.86, $C_{20}H_{14}O_5$ requires C, 71.86 ; H, 4.19%). It was found insoluble in alkali and did not give any colouration with alcoholic ferric chloride. IR 1650 cm^{-1} (>C=O).

Bi(2-methyl-3-acetyl-6-chromonyl) ether :

A mixture of 3,3'-diacetyl-4,4'-dihydroxy diphenyl ether (1.5 g) acetic anhydride (15 ml) and fused sodium acetate (6 g.) was refluxed in an oil bath for 10 hr. at 180-90°. The product obtained on pouring the reaction mixture in cold water was washed with dilute alkali and crystallised from alcohol, m.p. 212°, yield 0.6 g. (Found : C, 68.84 ; H, 4.70. $C_{24}H_{18}O_7$ requires C, 68.90 ; H, 4.30%). IR 1650 cm^{-1} (γ-pyronyl >C=O gr.) and 1680 cm^{-1} >C=O at 3 position).

4,4'-Di(β-cyanoethoxy) diphenyl ether :

A mixture of 4,4'-dihydroxy diphenyl ether (2 g.), acrylonitrile (5 ml.) and cupric oxide (0.2 g.) was refluxed for 25 hr. The reaction mixture was then treated with chloroform and the chloroform layer was washed with sodium hydroxide. The product obtained on removal of chloroform was crystallised from alcohol. m.p. 102°, yield 0.6 g. (Found : C, 70.31 ; H, 5.25, N, 9.01, $C_{18}H_{16}O_3N_2$ requires C, 70.03 ; H, 5.19 ; N, 9.08%).

4,4'-Di(β-carboxyethoxy)diphenyl ether :

A mixture of the above cyano derivative (1 g) was refluxed with conc. hydrochloric acid (20 ml) for 4 hr. The product obtained was purified by sodium bicarbonate treatment and crystallised from alcohol, m.p. 198°, yield 0.5 g. (Found : C, 62.63 ; H, 4.83, $C_{18}H_{18}O_7$ requires C, 62.79 ; H, 5.23%).

Bi(6-chromononyl) ether :

The above dicarboxylic acid (0.5 g) was heated with polyphosphoric acid (20 g P_2O_5 ; 10 ml *o*-phosphoric acid) in an oil-bath for 3 hr. at 120°. The product obtained was washed with sodium bicarbonate solution and water and crystallised from alcohol in yellow needing (0.2 g) m.p. 175°. (Found : C, 69.47, H, 4.77, $C_{18}H_{14}O_5$ requires C, 69.68 H, 4.41%).

Bi(6-chromonyl) ether :

A mixture of bi(6-chromanonyl) ether (0.25 g) in diphenyl ether and palladised charcoal (10% ; 0.2 g) was refluxed for 6 hr. The mixture was filtered hot. The product obtained on cooling was cryrtallised from alcohol, m.p. 218°, yield 0.1 g (Found : C, 70.66. H, 3.48, $C_{18}H_{10}O_5$ requires C, 70.60 ; H, 3.26%), IR 1640 cm^{-1} (>C=O).

Bi(4'-hydroxy-6-coumarinyl) ether :

A mixture of 3,3'-diacetyl-4,4'-dihydroxy diphenyl ether (1.5 g), diethyl carbonate (20 ml) and pulverised sodium (2 g) was heated on a steam bath for 10 hr. A little alcohol was added to decompose the unreacted sodium followed by cold water and the mixture was washed with ether and acidified. The

product was purified by extraction with sodium bicarbonate solution and crystallised from alcohol. m.p. 302° (decomp), (Found: C. 63.52; H, 2.88, $C_{18}H_{10}O_7$ requires C, 63.92; H, 2.95%).

3,3'-Diacetyl-4-4'-di(carbethoxymethoxy) diphenyl ether:

3,3'-Diacteyl-4,4'-dihydroxy diphenyl ether (1 g) was refluxed with ethyl bromoacetate (0.7 ml) in the presence of anhydrous potassium carbonate (5 g) in dry acetone for 5 hr. The product obtained on removal of acetone was washed with water and crystallised from alcohol in thin shining plates (0.6 g) m.p. 117°, (Found: C, 62.82; H, 5.69, $C_{24}H_{26}O_9$ requires C, 62.88; H, 5.67%).

3,3'-Diacetyl-4,4'-di(carboxymethoxy) diphenyl ether:

The above ester (1 g) was kept in sodium hydroxide solution (20 ml 10%) for the clear liquid on acidification gave a product which was extracted with sodium bicarbonate solution. The acid obtained was crystallised from alcohol, m.p. 176°, yield 0.4 g. (Found: C, 59.36; H, 4.86, $C_{20}H_{18}O_9$ requires C, 59.70; H, 4.47%).

Bi(3-methyl-5-benzofuranyl) ether

The above dicarboxylic acid (0.5 g) was refluxed with sodium acetate (1 g) and acetic anhydride (5 ml.) for 1 hr. The product obtained on pouring the reaction mixture in water was crystallised from alcohol in thick needles (0.2 g), m.p. 78°, (Found: C, 77.80; H, 5.32, $C_{18}H_{14}O_3$ requires C, 77.71; H, 5.03%.) IR. 885 cm^{-1} (Furan ring breathing) UV λ_{max} (chloroform) 258,290 nm.

3,3'-Diacetyl-4,4'-dibenzoyloxy diphenyl ether:

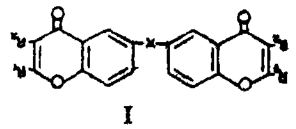
A mixture of 3,3'-diacetyl-4,4'-dihydroxy diphenyl ether (1.5 g) in pyridine, and benzoyl chloride (2 ml.) was kept at room temperature for 1.5 hr. The reaction mixture was treated with cold hydrochloric acid (1 : 1). The pasty mass was purified by washing with sodium bicarbonate solution and hot water. It crystallised from acetic acid m.p. 127°, yield 0.5 g (Found, C, 73.36, H, 4.66, $C_{30}H_{22}O_7$ requires C, 72.88, H, 4.46%).

3,3'-Di(benzoylacetyl)-4,4'-dihydroxy diphenyl ether:

A solution of the above benzoyloxy derivative (1.5 g) in pyridine was mixed with powdered potassium hydroxide (9 g) and kept for 4 hr. at room temperature. The product obtained on adding hydrochloric acid was extracted with sodium hydroxide solution. The product obtained on acidification crystallised from benzene, m.p. 163°, yield 0.8 g (Found: C, 72.49; H, 4.35, $C_{30}H_{22}O_7$ requires C, 72.88; H, 4.45%).

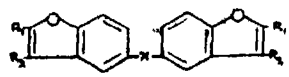
Bi(6-flavonyl) ether:

The above β-diketone derivaative (0.5 g) was mixed with conc. sulphuric acid and the reaction mixture was kept overnight. The product obtained on pouring the reaction mixture in water crystallised from acetic acid. m.p. 257°, yield 0.2 g (Found: C, 73 13. H, 4.29, $C_{30}H_{18}O_5.2H_2O$ requires C, 72.88; H, 4.45%), IR. 1645 cm^{-1} (>C=O group).



I

	X	R_1	R_2
a	SO_2	C_6H_5	H
b	O	CH_3	H
c	O	CH_3	$COCH_3$
d	O	H	H
e	O	C_6H_5	H



II

	X	R_1	R_2
a	SO_2	H	CH_3
b	SO_2	CH_3	H
c	O	H	CH_3

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Apparent Molal Volumes of some Common Salts in Acetone-water Mixture

K. SINGH*
Chemistry Department, B. S. N. V. Degree College, Lucknow, (U.P.), (India) and
P. P. SINHA
Lucknow Christian College, Lucknow, (U.P.)

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Dependence of apparent molal volume, ϕv, on composition of mixture have been examined using acetone-water mixtures as media of varying dielectric constant. The results indicate that the plots of ϕv vs $\sqrt{c}$ are almost straight line and have a positive slope for all the salts in all the mixture. The limiting apparent molal volume, ϕ°, obtained in the usual manner is found to be dependent on the solvent composition. The experimental results are expressed in terms of ion-solvent and ion-ion interactions together with role of dielectric constant of the medium.

IN continuation of our previous studies[1-5], the present work was undertaken to determine the effect of concentration and solvent composition on the apparent molal volumes, ϕv, of ammonium chloride, ammonium bromide and ammonium nitrate in 9.64%, 19.84% and 34.43% acetone-water mixtures at 25°. No previous work has been reported on the apparent molal volumes of these salts in acetone-water mixtures, although little work has been reported on apparent molal volumes in some other mixed solvents[6-10].

This is the aim of present work to use acetone-water mixture for examining the effect of dielectric constant and solvent composition on the apparent and limiting apparent molal volumes.

Experimental

The B. D. H. (A. R.) samples of common electrolytes were purified by repeated crystallisation from conductivity water. The purified samples were dried in a hot air oven and stored in vacuum desiccator.

Water used in all measurements was prepared by redistillation of distilled water containing a little potassium permanganate through block of condenser and having only middle fraction. The specific conductance of the sample used was 1.0×10^{-6} ohm^{-1} cm^{-1} at 25°. B. D. H, (A. R.) acetone was first distilled and middle part was collected. After keeping for 12 hours over potassium permanganate, the middle part was redistilled. The new distillate was kept overnight over anhydrous potassium carbonate and was redistilled, the purity of the sample was checked by density and refractive index measurements.

Stock solutions of acetone-water mixtures were prepared by calculating required volume using density data in a water thermostat running at 25± 0.005°. All solutions were prepared on molal basis.

The densities of the solutions were determined using dilatometer described in earlier communication[4]. Duplicate measurements was made for each solution and the average value is taken.

From the density data, apparent molal volume, ϕv, was calculated using the equation namely.

$$\phi v = \frac{1000\,(d_0 - d)}{m d\, d_0} + \frac{M}{d}$$

Where d_0 and d are the density of solvent and solution respectively, m is the molality of the solution, M is the molecular weight of the salt.

ϕv values were determined for each salt in each solvent composition over a concentration range of 0.1 to 0.4 m.

Results and Discussion

From the apparent molal volume, ϕv, values for different common salts in different acetone-water mixtures at 25°, ϕv vs. $\sqrt{c}$ curves have been drawn. An illustrative example of the plots are demonstrated for NH_4Cl in Fig. 1. These curves are almost straight lines and so the Masson's equation namely,

$$\phi v = \phi^\circ + Sv\sqrt{c}$$

appears to be valid within the concentration range studied here. The slope, Sv, of ϕv vs $\sqrt{c}$ curves for all the salts in all the mixtures under investigation is positive as reported in aqueous solution[11] and methanol-water mixture[5].

As the present data correspond to higher concentrations, it is not possible to use the data for testing the applicability of the Debye-Huckel limiting

*To whom all correspondence may be addressed.

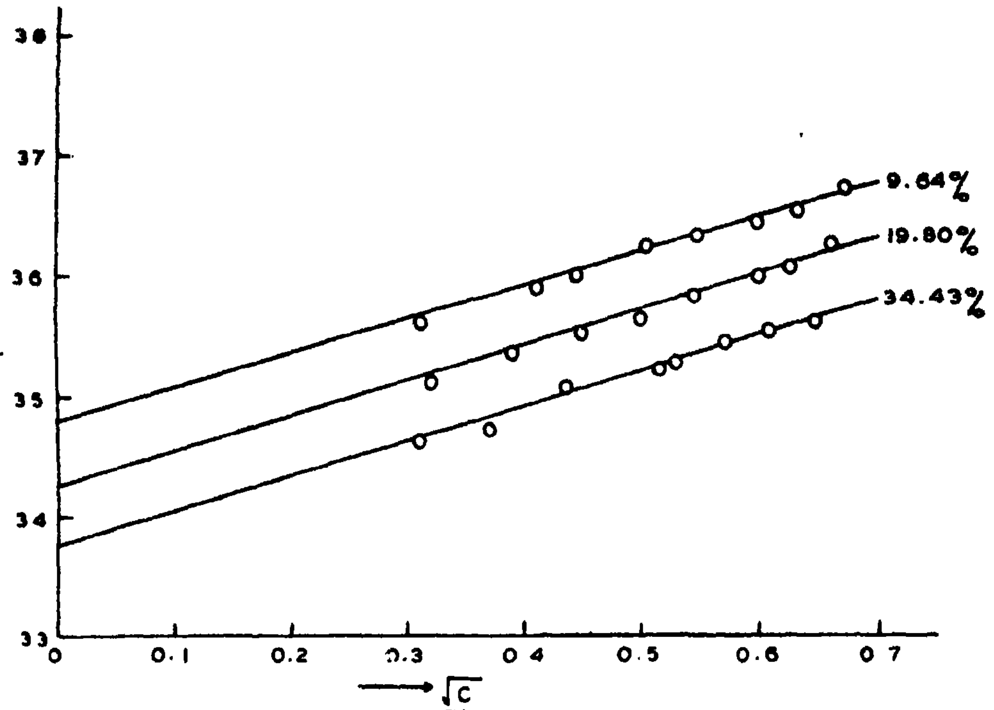


Fig. 1

law. It appears, therefore, reasonable not to attach too much quantitative significance to the Sv values and only dependence of apparent molal volume on concentration and composition should be used to throw light on the mode of ion-solvent and ion-ion interactions in acetone-water mixtures.

The positive slope of ϕv vs. $\sqrt{c}$ curves may be taken to be due to electrostatic ion-ion interaction which is enhanced in a medium of lower dielectric constant. The greatest value of ϕv in most concentrated solution indicates that extent of solvation for an individual ion is least due to increase in number of ions.

The limiting apparent molal volumes, ϕ°, obtained by extrapolating ϕv vs $\sqrt{c}$ curves of NH_4Cl, NH_4Br and NH_4NO_3 in different acetone-water mixtures are given in Table 1. From Table 1, it may be noted that ϕ° decreases with increase in the acetone contents of the mixture. which may be due to structuredness of water probably as result of hydrophobic interaction betweeu acetone and water.

TABLE—1 LIMITING APPARENT MOLAL VOLUME, ϕ°, OF SOME SALTS IN ACETONE-WATER MIXTURES AT 25°

Percent (by weight) of acetone in the mixture	ϕ° in ml mole^{-1} for NH_4Cl	NH_4Br	NH_4NO_3
9.64 ($\epsilon 25^{\circ}$=73.28)	34.80	42.30	47.15
19.80 ($\epsilon 25^{\circ}$=67.73)	34.25	41.70	46.60
34.43 ($\epsilon 25^{\circ}$=59.17)	33.75	40.95	46.00

From Table 1, it is also clear that dielectric constant of the mixed solvent decreases with increase in acetone content of the mixture. The limiting apparent molal volume, ϕ°, decreases with decrease in the dielectric constant of the medium. This decreasing trend appears reasonable since ionic association is favoured in the medium of lower dielectric constant and replacement of two ionic species by one.

Thus the general conclusion from the present study is that the smaller dielectric constant favours a smaller value of limiting apparent molal volume, ϕ°, as a result of weaker electrostatic ion-solvent interaction. With respect to have a more clear idea of dependence of ϕ° on composition of the solvent and dielectric constant of the medium, further investigations are in progress.

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New Indicators for the Direct HEDTA Titration of Ferric Ions

B. M. DESAI and MISS J. V. PARGHI

Chemistry Department, M. G. Science Institute, Ahmedabad-9

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The working conditions for the use of protocatechuic acid, 3-hydroxy 2-naphthoic acid and tiron as indicators for the direct HEDTA titration of ferric ions are reported. These indicators give a sharp colour change at the end point and can be used for microtitration of iron, the lowest permissible concentration being 0.056 mg/ml. A large number of diverse ions are tolerated. A procedure has been suggested for the determination of ferric ions when present alone in synthetic solutions, an ore and pharmaceuticals.

WHILE a number of substances investigated as indicators for the direct EDTA titration of ferric ions, no substances have been reported so far for the direct titration of HEDTA with ferric ions. The present article reports the use of protocatechuic acid, 3-hydroxy 2-naphthoic acid and tiron as indicators for the direct HEDTA titration of ferric ions. Protocatechuic acid and tiron give green colour with ferric ions, whereas 3-hydroxy 2-naphthoic acid gives a blue colour. When such a solution was titrated with HEDTA, the characteristic green or blue colour was discharged and at the end point, there was a sudden change to yellow. If a solution of HEDTA was titrated with ferric ions, there was a change from colourless to light green with tiron and protocatechuic acid and from colourless to light blue with 3-hydroxy 2-naphthoic acid.

Experimental

Ferric Nitrate Solution :

A stock solution of ferric nitrate (0.1 *M*) was prepared by dissolving 40.38 g of ferric nitrate nonahydrate in distilled water and making upto one litre. It was standardised gravimetrically as ferric oxide.

HEDTA solution :

A stock solution of 0.01*M* HEDTA was prepared by dissolving 2.78 g. of HEDTA in distilled water on heating and making upto one litre.

Indicator solutions :

1% solution were prepared from pure samples of the reagents by dissolving the requisite amount in 95% alcohol. The solutions were stable upto four weeks.

Metal solutions :

To study the interference of various foreign ions in the estimation of iron(III) with HEDTA, the corresponding analar quality of salts were taken and their 0.2 *M* solutions were prepared in distilled water.

Suggested procedure :

Take an aliquot of solution containing ferric ions, adjust the *p*H to 1.0-2.0 and add four drops of a 1% solution of the indicator. Titrate against standard HEDTA solution to a deep yellow colour.

Effect of pH :

It was found that when HEDTA solution was taken in burette, accurate results were obtained in the *p*H range 1.0 -2.8, at 0.01 *M* and 0.005 *M* concentrations of ferric ions. In case of 0.001 *M* concentrations of ferric ions accurate results were obtained in the *p*H range of 2.0 - 2.8. Outside these ranges, the accuracy of titration decreased. Further it should also be noted that at *p*H values less than 1.5, the colour intensity of ferric complex of the indicator decreased. It was thus advisable to add a higher amount of indicator in the *p*H range below 1.5.

If the ferric solution was taken in the burette accurate results were obtained over a wide *p*H range, i.e. to 1.0-9.0. However, the former process is more satisfactory because the colour change is more perceptible.

Effect of Indicator Concentration :

Titrations were carried out with different proportions of the indicator and it was found that an addition of 4 drops of 1% indicator solution in ethanol to 5 ml of titre solution gave accurate and sharp end point.

Effect of ferric ion concentration :

0.01 *M*, 0.005 *M*, 0.001 *M* and 0.0005*M* solutions of ferric ion were titrated with HEDTA using the suggested indicators. At 0.0005 M concentration of iron, the end point was not very sharp. However the titration of 1.0 ml volume of 0.001 M ferric nitrate could be accurately performed with a sharp end point. Thus microtitration of ferric ions with HEDTA is feasible with these indicators.

Effect of Temperature :

Titrations were carried out at three temperature ranges 0-5°, 30-35° and 55-60°. It was necessary to add slightly more indicator at lower temperature. Accurate results could be obtained at all the temperatures investigated.

Effect of Foreign Ions :

Synthetic solutions containing 2.8 mg iron(III) were titrated at *p*H 1.0 and 2.0 It was found that 100 fold amount of Na^+, K^+, NH_4^+, La^{3+}, Ca^+, Be^{2+}, UO_2^{2+}, Cl^-, Br^-, NO_3^- and SO_4^{2-}, 4 fold amount of Ca^{2+}, Ba^{2+} and Sr^{2+}, 2 fold amount of Zn^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+}, and equal amount of Pb^{2+}, Ag^+, Cr^{3+} and HCO_3^- could be tollerated (i.e. error $<1\%$) phosphate, fluoride oxalate, carbonate, iodide, thorium and zirconium interfered at all levels.

Analysis of Pharmaceuticals Containing Iron :

The suggested procedure was applied to the analysis of pharmaceuticals containing iron in the form of colloidal iron hydroxide, ferrous gluconate, ferrous fumarate and ferrous sulphate.

Liquid drugs containing ferrous sulphate or ferric hydoxide were diluted with distilled water, and 2.0 ml conc. HNO_3 was added. The mixture was heated for 10-15 minutes and after cooling, diluted to 100 ml.

Tablets or capsules of drugs containing ferrous sulphate, ferrous fumarate or ferrous gluconate were treated with 10 ml conc. HNO_3 and 2 ml. $HClO_4$. The mixture was evaporated to dryness. The residue was diluted to 50 ml aliquots of the dilute solution were used for titration. Results are given in table 2.

Ore :

2 g. of bauxite ore was fused with 10.0 g. of fusionmixture and treated with conc. HCl. 2 ml nitric acid was then added to oxidise ferrous ions to ferric ions, silica was filtered and the filtrate was diluted to 100 ml. 5.0 ml. diluted solution was used to estimate iron. The expected iron content was 2.86% Fe_2O_3 while the iron content found by above procedure was 2.8% Fe_2O_3.

TABLE—1 ANNLYSIS OF SYNTHETIC SOLUTIONS

*p*H of titration : 1.0 — Concentration of HEDTA : 0.01 *M*

Fe^{3+} taken (mg)	Foreign ions (mg)		Tiron	Fe^{3+} found (mg) Protocatechuic acid	3-hydroxy 2-naphthoic acid
2.8	Ca^{2+} 7.0,	Sr^{2+} 8.0	2.8	2.8	2.8
2.8	Ca^{2+} 8.0,	Ba^{2+} 7.0	2.8	2.8	2.8
2.8	Mg^{2+} 2.5,	Pb^{2+} 1.25	2.75	2.8	2.8
2.8	Zn^{2+} 2.5,	Mg^{2+} 2.5	2.8	2.8	2.8
2.8	Cd^{2+} 2.0,	Be^{2+} 25.0	2.8	2.8	2.8
2.8	K^+ 17.5,	NH_4^+ 22.5	2.8	2.8	2.8
2.8	La^{3+} 25.0,	Cs^+ 15.0	2.8	2.8	2.8
2.8	SO_4^{2-} 30.0,	NO_3^- 10.0	2.8	2.8	2.8
2.8	Cl^- 25.0,	Br^- 25.0	2.8	2.8	2.8
2.8	Co^{2+} 2.5,	Ni^{2+} 2.5	2 8	2.8	2.8

TABLE – 2 ANALYSIS OF DRUGS CONTAINING IRON BY DIRECT TITRATION WITH HEDTA

Drug trade name	State of the drug	Manufacture	Active constituent of the drug	Fe^{3+} expected (g)	Fe^{3+} Indicator Tiron	Found (g) Indicator Protocatechuic acid	Indicator 3-hydroxy-2-naphthoic acid
Polycytol	Tablet	Alembic Chemicals	Ferrous sulphate (dried)	0.195	0.194	0.194	0.194
Fersolate	Tablet	Glaxo Laboratory	Ferrous sulphate (dried)	0.195	0.194	0.191	0.194
Iberol	Tablet	Abbott Laboratory	Ferrous sulphate (hydrated)	0.525	0.522	0.522	0.522
Iberolliquid	Syrup	Abbott Laboratory	Ferrous sulphate (hydrated)	0.131	0.130	0.130	0.130
Livogen	Capsule	British Drug House	Ferrous fumarate	0.150	0.146	0.146	0.146
Ferrofolindione	Tablet	'Indopharma' Pharmaceuticals	Ferrous fumarate	0.200	0.197	0.193	0.197
Microfer	Tablet	Naphtha Pharmaceuticals	Ferrous gluconate	0.195	0.194	0.192	0.190
Tonoferon drops	Syrup	East India Pharmaceutical Works	Colloidal hydroxide	0.050	0.046	0.047	0.047

The above procedure was applied to the determination of ferric ions in synthetic solutions. Results are given in Table 1.

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Direct and Indirect Titrimetric Determinations of Thiocyanate Ion in Metal Salts and Complexes using Lead Tetraacetate

B. T. GOWDA AND D. S. MAHADEVAPPA

Department of Post-graduate Studies and Research in Chemistry, University of Mysore
Manasa Gangotri, Mysore-570006.

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A simple but rapid and accurate method of determining thiocyanate ion in metal salts and complexes by a direct titration with lead tetraacetate in presence of sodium acetate and KBr has been developed. The direct titration with a visual or potentiometric end point involves an eight electron change per thiocyanate ion. A back titration procedure in which thiocyanate ion in metal salts and complexes undergoes a six electron change in presence of sodium acetate has been reported. A method for estimating cyanide and thiocyanate ions in mixtures is also described. The proposed analytical methods are useful for a rapid estimation of thiocyanate ion in metal salts and complexes on a macroscale and also for computing the number of ligand molecules present in a thiocyanate complex.

RAPID analytical techniques are essential for estimating thiocyanates, as they find a number of industrial applications such as in photography, printing and dyeing textiles, in the manufacture of synthetic dyestuffs, other sulfocyanides, thioureas and mustard oil, in medicine and freezing mixtures and as a reagent in analytical chemistry. The methods reported so far include the use of hypohalite[1], bromine,[2] iodine,[3] iodate,[4] H_2O_2[5] and chloramine-T[6-10] which involve mostly back titration procedures.

Lead tetraacetate (LTA, or $PbAc_4$) is a versatile oxidant, commonly employed as a reagent in preparative organic chemistry. Its solution in glacial acetic acid is generally employed for oxidation purposes. The redox potential of Pb^{4+}/Pb^{2+} is about 1.40 V in presence of perchloric acid and is about 1.30 V in presence of sodium acetate. The presence of water accelerates most of the oxidations carried out with LTA if the solution contains sodium acetate. An important advantage of using LTA is the rapid and quantitative oxidation of substrates in presence of sodium acetate and some of the analytical procedures are so sensitive that very small amounts of compounds can be estimated accurately.

In the present investigations, we have critically examined the oxidation of thiocyanate ion in metal salts and complexes, by LTA. We have proposed (i) a rapid method for estimating thiocyanate ion by a direct titration with the oxidant in presence of KBr and sodium acetate, with a visual or potentiometric end point and (ii) a rapid back titration procedure in presence of sodium acetate. An eight electron and a six electron stoichiometry are observed in the two cases respectively. It was found that macro amounts of CNS^- ion can be estimated by a proper adjustment of reaction conditions. Further, the method can be extended for estimating thiocyanate and cyanide ions in a mixture.

Materials and Methods

Triply distilled water was used in preparing the solutions. A. R. grade KCNS (E.Merck) was dried at 150° for two hours and its purity was checked.[4] Metal thiocyanates NaCNS, $Cd(CNS)_2$, $Zn(CNS)_2$, $Ni(CNS)_2 \cdot 0.5\ H_2O$, $Ba(CNS)_2.2H_2O$, $Pb(CNS)_2$, $UO_2(CNS)_2 \cdot 3\ H_2O$ and complexes $K_4Pb(CNS)_6$, $KUO_2(CNS)_3.2H_2O$, $K_2Zn(CNS)_4.4H_2O$, $K_2Cd(CNS)_4.2H_2O$ and $K_4Ni(CNS)_6.4H_2O$ were prepared by standard methods. The compounds were recrystallised from aqueous solution and their composition was checked by elemental analyses. Solutions of the compounds (~2mg/ml) in water or dilute acetic acid (only lead compounds) were prepared. Lead tetraacetate (Riedel) was used without further purification. An approximately decinormal solution of the compound in glacial acetic acid was prepared, standardised by the iodometric method and stored in an amber coloured bottle. All other materials and reagents were of accepted grades of purity. A Bajaj potentiometer with a platinum indicator electrode and a reference calomel electrode was used for potentiometric titrations.

I. *Direct titration*

Method 1

(a) *Visual end point :* A direct titration of thiocyanate solution with LTA was found practicable in presence of sodium acetate and KBr, the former to accelerate the decomposition of LTA. The oxidant liberates bromine from KBr, which in turn oxidizes

thiocyanate ion while at the same time serving as an indicator to detect the end point in an Andrews type of titration, employing carbon tetrachloride.

Recommended procedure : Take aliquots of thiocyanate solution in a 100 ml conical flask. Add 10 ml of 20% sodium acetate, 10 ml of 1 N KBr and 1 ml of CCl_4 and titrate against LTA with shaking till the appearance of a faint yellow colour in CCl_4 layer. Blank correction was found to be about 0.05 ml of 0.1N LTA.

(b) *Potentiometric end point* : A potentiometric titration of thiocyanate with LTA was possible in presence of sodium acetate (10 ml of 20% solution) and KBr (10 ml of 1N solution). A large potential jump of ~300-500 mV was noticed for the addition of 0.1 ml of 0.1N oxidant at the equivalence point. In the absence of KBr, no potential break was found in most cases, while small potential jumps of the order of 100 mV occurred with a few thiocyanates, which however did not correspond to any definite stoichiometry.

Method 2

Blank correction and pipetting of the poisonous thiocyanate solutions can be avoided if the procedure of method 1 is reversed, by adding reductant to the oxidant. Volatility of bromine is the only source of error under these conditions, which however can be minimised by a proper choice of the titration assembly.

(a) *Visual end point* : Take aliquots of LTA solution in a 100 ml (two holed) stoppered conical flask. Add 10 ml of 20% sodium acetate, 10 ml of 1 N KBr and 1 ml of CCl_4 through a dropping funnel and titrate with thiocyanate solution with stirring slowly till the disappearance of bromine colour in CCl_4 layer.

(b) *Potentiometric end point* : A large potential jump of ~300-500 mV was noticed for the addition of 0.1 ml of ~0·03M reductant at the equivalence point in presence of 10 ml of 20% sodium acetate and 10 ml 1N KBr.

II. *Back titration*

In preliminary investigations, known amounts of thiocyanate solution were added to a known excessive volume of LTA in presence of sodium acetate in an iodine flask. The reaction mixture was set aside for various intervals of time at room temperature with occasional shaking. The excess LTA left unconsumed was iodometrically determined with standard thiosulphate. It was seen that stoichiometric oxidation of thiocyanate ion in the metal salts and complexes with a reproducible six electron change per thiocyanate ion took place in 5 minutes with a 40-50% excess of LTA. With a 10-20% excess the reaction is complete after 30 minutes.

Recommended procedure : Prepare a solution of salt or complex thiocyanate (~2 mg/ml) in water or dilute acetic acid. Add aliquots of the solution to a known excessive volume of 0.1N LTA (~40-50% excess) in an iodine flask also containing 10 ml of 20% sodium acetate, shake the contents and set aside for 5 minutes. Add 10 ml each of 20% potassium iodide and titrate the liberated iodine against 0.1N sodium thiosulphate. Run a blank with LTA alone.

Results and Discussion

The eight electron stoichiometry found in direct titration procedures is indicated below, by assuming the in situ liberation of bromine from KBr by the oxidant.

$$Pb^{4+} + 2Br^- \longrightarrow Pb^{2+} + Br_2 \quad \ldots \quad (1)$$

$$CNS^- + 4Br_2 + 4H_2O \longrightarrow SO_4^{2-} + CNBr + 8H^+ + 7Br^- \quad \ldots \quad (2)$$

Bromine cyanide formed could be quantitatively estimated by the iodometric method.[11]

It is seen from equations (1) and (2) that stoichiometric quantities of KBr are required for a quantitative oxidation of thiocyanates.

The six electron stoichiometry observed for the oxidation of thiocyanate ion during the back titration procedure can be shown as follows :

$$CNS^- + 3Pb^{4+} + 4H_2O \longrightarrow 3Pb^{2+} + SO_4^{2-} + 8H^+ + CN^- \ldots (3)$$

The presence of CN^- in the reaction products was detected by spot tests.[12]

The results of analyses are shown in Table 1. It shows the range of amounts of thiocyanate employed and the percent error noted in the recovery. Each range covers the amounts present in 8-10 different aliquots of the compound. Further, as a comparison the results of analyses by the argentometric method[13] are included in Table 1. It is seen that the maximum error encountered in the present method is about 0.5% while the silver nitrate method[13] shows an error up to 1.2% in the estimation of complex thiocyanates.

Common anions such as sulphate, phosphate, nitrate, perchlorate and fluoride do not interfere, but cyanide and iodide ions interfere in direct titration and chloride and bromide ions in the back titration.

Estimation of thiocyanate and cyanide in a mixture :

The fact that cyanide ion does not interfere in the back titration method but is oxidised by LTA in

TABLE—1 TITRIMETRIC DETERMINATION OF THIOCYANATES WITH LEAD TETRAACETATE

Compound	Range studied (mg)	LTA % error in recovery Direct titration : Method 1			AgNO$_3$	Range studied (mg)	% error in recovery Direct titration : Method 2	
		Visual end point	Potentio-metric end point	Back titration			Visual end point	Potentio-metric end point
KCNS	2.22-111.00	0.01-0.54	0.09-0.45	0.00-0.43	0.00-0.59	1.36-108.86	0.00-0.44	0.00-0.51
NaCNS	1.88-112.69	0.00-0.32	0.00-0.54	0.00-0.27	0.00-0.27	1.71-102.55	0.00-0.58	0.00-0.58
$Cd(CNS)_2$	1.80-108.00	0.00-0.55	0.06-0.55	0.06.0.55	0.00-0.60	2.41- 96.32	0.02-0.42	0.17-0.42
$Ni(CNS)_2 0.5H_2O$	0 93- 92.75	0.00-0.54	0.00-0.54	0.00-0.54	0.00-0.39	2.53-126.60	0.09-0.40	0.00-0.39
$Pb(CNS)_2$	2.00-100.16	0.00-0.50	0.00-0.30	0.20-0.52	0.00-0.50	1.67-133.65	0.03-0.60	0.00-0.48
$Zn(CNS)_2$	1.56-124.74	0.00-0.51	0.00-0.26	0.00-0.32	0.00-0.58	1.88- 93.82	0.00-0.53	0.08-0.53
$Ba(CNS)_2 2H_2O$	1.00-100.00	0.00-0.35	0.00-0.35	0.00-0.50	0.00-0.60	1.01-101.36	0.00-0.49	0.00-0.49
$UO_2(CNS)_2.3 H_2O$	2.41-120.72	0.00-0.41	0.00-0.21	0.08-0.42	0.41-1.03	1.27-126.81	0.00-0.51	0.00-0.51
$K_2 Zn(CNS)_4 4H_2O$	1.07-128.42	0 00-0.56	0.00-0.47	0.00-0.51	0.47-1.17	1.30-103.76	0.00-0.46	0.04-0.46
$K_2 Cd(CNS)_4 2H_2O$	2.03-101.55	0.07-0.49	0.00-0.49	0.20-0.50	0.00-1.08	1.32-105.16	0.00-0.15	0.00-0.53
$K_4 Ni(CNS)_6 4H_2O$	2.04-101.80	0.05-0.49	0.00-0.37	0.00-0.49	0.00-1.19	1.22- 97.60	0.00-0.29	0.00-0.29
$KUO_2(CNS)_3.2H_2O$	1.00-100.50	0.00-0.25	0.00-0 50	0.00-0.35	0.00-1.00	1.00- 99.70	0.00-0.50	0.00-0.50
$K_4 Pb(CNS)_6$	2.03-101.35	0.00-0.52	0.18-0.50	0.00-0.50	0.28-0.74	2.73-109.36	0.07-0.37	0.00-0 37

TABLE—2 TITRIMETRIC DETERMINATION OF THIOCYANATE AND CYANIDE IONS IN A MIXTURE WITH LEAD TETRAACETATE

Visual end point				Potentiometric end point			
CNS^- (mg)		CN^- (mg)		CNS^- (mg)		CN^- (mg)	
Amount taken	Amount found	Amount taken	Amount found	Amount taken	Amount found	Amount taken	Amount found
0.85	0.85	1.13	1.12	0.84	0.84	1.12	1.12
2.12	2.12	2.81	2.80	2.10	2.10	2.80	2.79
4.20	4.22	5.60	5.60	4.24	4.23	5.65	5.63
8.44	8.46	11.25	11.22	8.40	8.42	11.20	11.22
16.80	16.88	22.40	22.47	16.88	16.87	22.50	22.54
33.68	33.76	44.90	44.94	33.76	33.84	45.00	44.81
67.52	67.59	90.00	89.76	67.36	67.68	89.80	89.62
84.45	84.50	112.60	112.16	84.53	84.43	112.70	112.29

a direct titration in presence of KBr with a 2-electron change[10] can be utilized for estimating thiocyanate and cyanide ions in a mixture. An aliquot of the LTA solution (V_1 ml) is directly titrated against CN^- and CNS^- ion mixture as in method 2 (V ml). Then the amount of thiocyanate ion in 'V' ml of the mixture is determined by back titration with LTA. Let the volume of LTA consumed by thiocyanate ion in 'V' ml of the mixture be V_2 ml. The amounts of thiocyanate ion (x mg) and cyanide ion (y mg) in the reaction mixture are given by

$$x = 9.68 \; N V_2 \text{ and}$$

$$y = 13 \; N \left(V_1 - \tfrac{8}{9} V_2\right)$$

where 'N' is the normality of LTA.

Some typical results of analyses are shown in Table 2.

It may be concluded that the proposed analytical techniques are useful for a computation of the number of ligand molecules present in a thiocyanate complex and for estimating cyanide and thiocyanate ions in mixtures.

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Heterocyclic-azo-dyes as Visual Indicators in the Titration of Ferrocyanide with Zinc

J. P. GUPTA, B. S. GARG and R. P. SINGH
Department of Chemistry, University of Delhi, Delhi-110007

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Suitability of some heterocyclic azo dyes viz. AHP-4S, DHP-4S and CPD-4S has been examined in the titration of ferrocyanide with zinc. Colour change at the end point is orange to magenta. The studies have been made at room temperature. Interference due to diverse ions have been studied in detail. Statistical evaluations of each titrations have also been carried out.

ON addition of ferrocyanide ion to zinc(II) solution, a white precipitate of $Zn_2Fe(CN)_6$ is formed, which is converted by excess of the reagent into less soluble[1] $K_2Zn_3[Fe(CN)_6]_2$.

$$2\,ZnSO_4 + K_4Fe(CN)_6 \rightleftharpoons Zn_2Fe(CN)_6 + 2K_2SO_4$$
$$3Zn_2Fe(CN)_6 + K_4Fe(CN)_6 \rightleftharpoons K_2Zn_3[Fe(CN)_6]_2$$

The traditional procedure for the determination of end point of the reactions utilizes uranyl nitrate and ammonium molybdate as external indicators. Numerous internal indicators such as diphenylamine, diphenylbenzidine, diphenylbenzidine sulphonate, *o*-dianisidine, naphthidine, 3,3′-dimethylnaphthidine, *p*-ethoxychrysoidine have been proposed as redox indicators[2]; quinine sulphate[3] and 8-quinol-5-sulphonic acid[3] as a fluorescence indicators; dithiozone in carbon tetrachloride and ferric ion as colour indicators andmethyl red as an adsorption indicator have also been used.

In the present communication three different heterocyclic-azo-dyes have been used successfully as visual indicators for the titrimetric determination of ferrocyanide using zinc (II) sulphate as the titrant. These reagents have already been utilized for the complexometric determination of zinc(II), cadmium(II), mercury(II)[4] and copper(II), cobalt(II), nickel (II)[5]. The formation of these dyes has been made use in determination of nitrite[6].

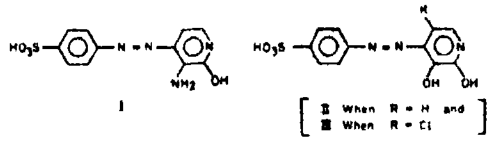
Experimental

Reagents :

Standard Zinc(II) Sulphate Solution was prepared by dissolving requisite amount of zinc sulphate heptahydrate (B.D.H.,A.R.) in doubly distilled water followed by addition of few drops of dilute sulphuric acid and standardized complexometrically using ELTA as titrant and Eriochrome Black T as indicator.

Standard Potassium Ferrocyanide Solution was prepared by dissolving appropriate amount of potassium ferrocyanide (B.D.H., A.R.) in doubly distilled water.

Dye Solution : 0.25% (w/v) solutions of the dyes in doubly distilled water were used throughout the study. The dyes were isolated by diazotizing sulphanilic acid and subsequently coupling the resulting diazotized product with three different substituted hydroxypyridines viz., 2-amino-3-hydroxypyridine (AHP), 2,3-dihydroxypyridine (DHP) and 5-chloropyridine-2, 3-diol (CPD). On the basis of elemental analysis and colour reactions which they give with metal ions, following tentative structures have been assigned to the dyes.



(I) 1-(2-amino-3-hydroxy-4-pyridylazo)-benzene-4-sulphonic acid (AHP-4S)

(II) 1-(2,3-dihydroxy-4-pyridylazo)-benzene-4-sulphonic acid (DHP-4S)

(III) 1-(5-chloro-4-pyridylazo-2, 3-diol)-benzene-4-sulphonic acid (CPD-4S)

Recommended Procedure :

To a suitable aliquot containing 0.2-10.6 mg of ferrocyanide ion, add 5 ml of pyridine buffer of *p*H 8.0 and 0.1-0.3 ml of 0.25% indicator solution (AHP-4S, DHP-4S or CPD-4S). Dilute the solution approximately to 20 ml by adding doubly distilled water and titrate at room temperature (27°) with shaking against standard zinc(II) sulphate solution ($1 \times 10^{-2} M$) taken in a micro burette till a sharp colour change (orange to magenta) is obtained. Titrations in reverse order can also be performed with equal accuracy and ease.

For accurate results, the amount of ferrocyanide should be taken between 0.2-10.6 mg.

Titrations in the presence of diverse ions :

To explore the possibility of performing these titrations in the presence of various interfering ions (anions and cations), titrations were performed by taking 4.24 mg of ferrocyanide and adding foreign ions in varying proportions and following the recommended procedure as given above. Masking agents were also used to undo some of the interferences of the cations Table 1.)

TABLE—1 INTERFERENCE OF DIVERSE IONS

Interfering ions	With AHP-4S, PPM	With DHP-4S, PPM	With CPD-4S, PPM	Masking Agent, if any
F′, Cl′, Br′, I′	5,000	5,000	5,000	-
NO_3, NO_2'	5,000	5,000	5,000	-
SO_4'', SO_3''	5,000	5,000	5,000	-
Acetate	5,000	5,000	5,000	-
ClO_4'	5,000	5,000	5,000	-
Citrate, Tartrate	5,000	5,000	5,000	-
Thiourea	5,000	5,000	5,000	-
C_2O_4''	5,000	500	100	-
S_2O_3''	500	500	500	-
BO_3'	Interferes	500	500	-
CNS′	300	300	100	-
S_2O_8''	5,000	2,000	1,000	-
Ti(IV)	240	240	240	-
Sb(III)	609	1,218	609	-
Pd*(II)	32	10	10	I′
W(VI)	5,000	5,000	5,000	-
Ge(IV)	100	100	100	-
V(V)	51	31	5	-
Sr(II)	5,000	5,000	5,000	-
Pb(II)*	21	8	21	I′
Sn(II)*	50	50	50	F′
Ti(I)	5,000	5,000	5,000	-
In(III)	230	12	23	-
Hg(II)*	10	50	100	I′
Ru(III)	20	20	20	-
Cd(II)*	2.2	2.2	2.2	I′
Mn(II)	5.5	5.5	2.8	-
Fe(II)	11	5	Interferes	-
Ir(III)	10	10	10	-
La(III)	28	28	14	-
Pr(III)	14	14	14	-
Y(III)	71	18	18	-
Yb(III)	35	17	17	-
Rh(III)	25	25	30	-
Ag(I)*	1,000	1,000	1,000	I′
Al(III)*	51	34	34	F′

*Metal ions masked with anions indicated in the last column. However, PO_4''', S′′, CN′, Cu(II), Co(II), Ni(II), Os(VIII) and Ce(III) interferes very seriously even in traces.

To check the precision and accuracy of the methods six identical solutions of ferrocyanide were titrated against zinc(II) solution using each of the above indicators. Statistical evaluation of the results are summarised in Table 2.

Results and Discussion

The various factors such as effect of indicator concentration, concentration of the metal ion, *p*H and temperature were investigated and optimum conditions for accurate titration of ferrocyanide with zinc(II) solutions using AHP-4S, DHP-4S and CPD-4S have been established. Attempts have also been made to determine ferrocyanide in the presence of large number of diverse ions, through masking etc. (Table 1). Statistical evaluation of the resuls were also carried out on the basis of six titrations under identical conditions (Table 2).

J. C. Bailer et al.[1] have assumed the ferrocyanide : zinc ratio either 1 : 2 or 2 : 3 corresponding to the species $Zn_2Fe(CN)_6$ or $K_2Zn_3[Fe(CN)_6]_2$. In our case, the ferrocyanide : zinc ratio is 1 : 2, which corresponds to the species $Zn_2Fe(CN)_6$, a white precipitate sparingly soluble in water.

Titrimetric determination of ferrocyanide using AHP-4S, DHP-4S and CPD-4S as visual indicators in pyridine buffer, with zinc(II) sulphate solution as titrant, is rapid and reliable. The colour changes at the end points are sharp and instantaneous. No indicator correction is required. All the titrations can be performed at room temperature (27°)

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TABLE—2 TITRATION OF FERROCYANIDE ,WITH ZINC(II) SULPHATE USING AHP-4S, DHP-4S AND CPD AS VISUAL INDICATORS

Indicator	Ferrocyanide taken in mg	Standard deviation	Variation coefficient	Relative width of confidence interval at 95% ($\alpha = 0.5$)	Relative Error m%
AHP-4S	4.24	0.024	0.57	4.24±0.025	0.42
DHP-4S	4.24	0.019	0.45	4.24±0.020	0.33
CPD-4S	4.24	0.024	0.57	4.24±0.025	0.42

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Determination of Sulphur Functions with *o*-Diacetoxy Iodobenzoate

ASHUTOSH SRIVASTAVA*, KRISHNA K. VERMA, JAMEEL AHMED AND SAMEER BOSE

Department of Chemistry, University of Jabalpur, Jabalpur-482001

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Procedures are evolved for the determination of some sulphur containing functional groups. *o*-Diacetoxy iodobenzoate is proposed and used as an analytical reagent for the determination of mercaptans, thioureas, organic sulphides, disulphides in dilute acetic acid medium and organic derivatives of dithiocarbonic acid at *p*H 7. The accuracy of the determination of mercaptans is 0.2%, of thioureas 0.5%, organic sulphides and disulphides 0.4%, and of organic derivatives of dithiocarbonic acid 0.5%. All the four methods are precise to 0.2-0.5%.

AMONG all compound of halogens, iodoso compounds are peculiar to iodine only. Similar compounds of other halogens either do not exist at all or are too unstable to be used as analytical reagents. The peculiarity of iodoso compounds lies in the fact that the iodine, even though in a positive oxidation state, must be linked to a carbon atom attached to a double bond. No stable compounds of positive iodine are known containing comparatively electro-positive saturated aliphatic radicals.

Hellerman et al[1] devised a method for determining cysteine with *o*-iodosobenzoate. But when this was applied to enzymes, inactivation was noticed. Finally, Hellerman opined that inactivation of enzymes could result from competitive inhibition by benzoate moiety rather than any effect of -SH groups. In the course of a systematic study on the determination of sulphydryl compounds consideration was given to the behaviour of a series of iodoso compounds. Thus, *o*-diacetoxy iodobenzoate was synthesized and a stoichiometric relationship for the oxidation of mercaptans in dilute acetic acid medium was established.

$$2RSH+(AcO)_2I{-}C_6H_4{-}COOK \rightarrow RSSRI+{-}C_6H_4{-}COOK+2HOAc$$

The reaction is immediate and can be used for the direct titration of mercaptans. This aroused a great deal of interest with a view to find out its possible application in the field of other sulphur functions.

o-Diacetoxy iodobenzoate can also be employed for the quantitative oxidation of thioureas in 80-30% acetic acid medium; corresponding urea and sulphate ion are the reaction products.

$$RNHCSNH_2+4(AcO)_2I{-}C_6H_4{-}COOK+5H_2O \rightarrow RNHCONH_2+KHSO_4+4I{-}C_6H_4{-}COOH+8HOAc$$

where, R=alkyl or Aryl group.

Thiosemicarbazide reacts as follows :

$$NH_2CSNHNH_2+5(AcO)_2I-C_6H_4-COOK+4H_2O \rightarrow KHSO_4+N_2+HCN+5I-C_6H_4-COOH+10HOAc$$

Determination of organic sulphides and disulphides by the procedure of Siggia *et al*[2] yields reliable results. But with coloured sample and crude materials, the end point is indistinct since appearance of first permanent bromine coloration is taken as the end point. The results are vitiated by the presence of a large amount of mercaptans because bromine oxidation of mercaptans is somewhat non-stoichiometric. *o*-Diacetoxy iodobenzoate stoichiometrically oxidizes disulphides in dilute acetic acid ; alpha-disulphone probably being the reaction products.

$$RSSR+4(AcO)_2I-C_6H_4-COOK+4H_2O \rightarrow RSO_2.SO_2R+4I-C_6H_4-COOK+8HOAc$$

Samples were treated with an excess of *o*-diacetoxy iodobenzoate in 30-80% acetic acid medium. The residual oxidant was determined by adding a measured excess of mercaptoacetic acid (it reacts in a molar ratio of 2 : 1 with *o*-diacetoxy iodobenzoate) followed by a back titration with standard iodine.

The same procedure is applied to determine organic sulphides, which are oxidized to sulphoxides.

$$RSR+(AcO)_2I-C_6H_4-COO+H_2O \rightarrow RSOR+I-C_6H_4-COOK+2\ HOAc$$

* Dr. Ashutosh Srivastava, 171, Bhaldarpura, Jabalpur-482002.

As high as 3-fold excess of the oxidant does not cause high results. Mercaptans, if present, cause serious interference in the determination of sulphides and disulphides. They are to be determined separately and the results be corrected for. In the present procedure sulphide or disulphide samples containing mercaptans are determined by first evaluating the mercaptan by the procedure described before. An identical sample is then titrated with *o*-diacetoxy iodobenzoate to the first ascertained titre in the absence of any starch-iodide so as to convert mercaptan into the disulphide ; the total sulphide and disulphide is finally estimated. The amount of disulphide produced by the oxidation of mercaptan is subtracted out of the total value to get sulphide or disulphide originally present.

A new oxidimetric procedure is evolved for determining organic derivatives of dithiocarbonic acid involving oxidation with *o*-diacetoxy iodobenzoate at *p*H 7 thereby converting them to corresponding dixanthogens.

$$2ROCS.SK+(AcO)_2I-C_6H_4-COOK+H_2O \rightarrow (ROCS.S\text{-})_2+I-C_6H_4-COOK+2AcOK$$

This procedure has also been applied to evaluate carbon disulphide involving conversion to xanthate with potassium ethoxide and determination of xanthate formed with *o*-diacetoxy iodobenzoate.

$$CS_2+C_2H_5OK \rightarrow C_2H_5OCS.SK$$

Xanthate formation according to the above equation is quantitative in the absence of water.

Experimental

Reagents and Samples

Preparation of o-diacetoxy iodobenzoic acid :

A mixture of 70 ml of 30% hydrogen peroxide and 305 ml of acetic anhydride was stirred for 4 hrs at 40°. *o*-Iodobenzoic acid 60.7 g, was then added to the solution which was stirred for further an hr and kept overnight. Some *o*-diacetoxy iodobenzoic acid separated out and was filtered. The filtrate on concentration to a small volume under reduced pressure (70 mm) yielded a second crop. The combined needle shaped crystals were washed with ether and dried (over NaOH) in a vacuum desiccator, yield 63.0 g. m.p. 206°.

o-Diacetoxy iodobenzoate solution (0.05*N*) was prepared by addition to the solid sample of the reagent of a slight excess of 1*N* potassium hydorxide solution and finally diluting upto the mark. It was standardized iodimetrically. A 0.01*N* solution was made by diluting the concentrated reagent with water.

o-Diacetoxy iodobenzoate solution (0.05*M*) was prepared by dissolving an appropriate amount of sample in glacial acetic acid and was standardized iodimetrically.

Phosphate buffer (*p*H 7) was prepared by dissolving 117.7 g of K_2HPO_4 and 44.1 g of KH_2PO_4 in 1 litre of water.

Most of the mercaptans, substituted thioureas and all derivatives of dithiocarbonic acid were prepared and purified by the authors.

A C.P. grade carbon disulphide was used.

Procedure for determining mercaptans :

A Sample containing 0.1-0.5 meq of mercaptan was weighed into a 150-ml Erl enmeyer flask containing 50 ml of distilled water. Sample, if insoluble in water, was dissolved in 10-15 ml of 99% acetic acid and at the time of titration sufficient water was added to bring acid concentration roughly 40-30% v/v. Less water may be used if sample comes out badly (at high acetic acid concentrations, reaction is slow and the end point is not of the sharpest type). About 50 mg of potassium iodide and 1 ml of 1% starch solution were added and the solution titrated with 0.01*N* *o*-diacetoxy iodobenzoate when upto 0.2 meq of mercaptan was present and 0.05*N* reagent solution was used for larger sample size. The end point is shown by a blue colour of starch-iodine.

Procedure for determining thioureas :

An aliquot of the sample, dissolved in water or 99% acetic acid, containing 0.01-0,1 meq of thiourea, was pipetted into a 250-ml Erl enmeyer flask. Acetic acid solution of 0.05*M* *o*-diacetoxy iodobenzoate was added, about 50% in excess. Prior to the addition of *o*-diacetoxy iodobenzoate calculated volumes of water were added to keep acid concentration between 80-30% v/v. Flask was kept aside for at least 30 mins. Thereafter, a measured excess of 0.05*M* solution of mercaptoacetic acid and 3 ml of 1*M* sulphuric acid were added and after 30 sec the residual amount of mercaptoacetic acid was titrated with 0.04*N* solution of iodine to a starch-iodine b lue colour. Concurrently, a blank determination was also carried out.

Procedure for determining sulphides and disulphides:

A sample containing 0.1-0.5 mmole of sulphide or 0.02-0.08 mmole of disulphide was weighed into a 250-ml Erl enmeyer flask and dissolved in 15-20 ml of 99% acetic acid. A 0.05*M* solution of *o*-diacetoxy iodobenzoate was added about 50% in excess along with calcuated volumes of distilled water so as to adjust acid concentration between 30-80%, v/v (reactions are slow in anhydrous acetic acid and catalysed moderately by water. Less water was used when the sample precipitates out). Flask was left for at least 20 mins (40 minutes in the case of methi-

onine and overnight when cystine was being determined) after which a measured excess of 0.05*M* solution of mercaptoacetic acid and 3 ml of 1*M* sulphuric acid was added and the contents swirled. The residual amount of mercaptoacetic acid was back titrated with 0.05*N* iodine solution using starch as indicator.

A blank determination was also run separately.

Procedure for determining organic derivatives of dithiocarbonic acid :

A sample containing 0.1-1.0 meq of sodium or potassium salt of dithiocarbonic acid was weighed into a 150-ml Erl enmeyer flask and dissolved in 10 ml of water. After which 5 ml of phosphate buffer, and 10 ml of suitably diluted aqueous solution of *o*-diacetoxy iodobenzoate was added so that it was about 50% in excess. The contents were swirled for 30 sec and then a measured excess of 0.05*M* solution of mercaptoacetic acid and 3 ml of sulphuric acid were added. After swirling for 30 sec the residual mercaptoacetic acid was titrated with 0.04*N* iodine solution to a starch-iodine blue colour.

A blank determination was also carried out in the same way.

Procedure for determining carbon disulphide :

A sample containing 0.1-1.0 mmole of carbon disulphide was weighed in a small sealed glass bulb and placed beneath a mixture of 0.5-2.0 ml of freshly prepared 10% potassium ethoxide and 5 ml of absolute ethanol contained in a 150 ml Erl enmeyer flask. A sharp rap against the side of the flask was sufficient to break the bulb and to release the sample. The contents were swirled for 2 mins and the flask was cooled in an ice bath. Thereafter 20 ml of water and 2-3 drops of phenolphthalein indicator were added and the base content was titrated with 1*M* acetic acid until the solution was just acid to the indicator. A suitable volume of phosphate buffer (*p*H 7) and 10 ml of *o*-diacetoxy iodobenzoate solution were added. The excess of the oxidant was determined after 30 secs using the method described before.

A blank determination was also carried out.

Results and Discussions

Results for the determination of several mercaptans Table 1 show that the method is sufficiently accurate. Cysteine, 3-mercaptopropionic, *o*-mercaptobenzoic and mercaptosuccinic acids are over-oxidixed and the present method is not recommended for them. Results for determining thioureas Table 2 showed excellent agreement with the amount of sample taken especially when dilute solutions were used. Diphenylthiourea does not react stoichiometrically. Quantitative results for the analysis of pure as well as crude samples of sulphide

TABLE—1 DETERMINATION OF MERCAPTANS WITH *o*-DIACETOXY IODOBENZOATE

Mercaptan titrated	Purity, % Present Method[a]	Comparison method	
Ethanethiol	100.1	99.8	Iodimetry[3]
Glutathione	98.0	98.1	Iodimetry[4]
p-Chlorobenzenethiol	96.2	96.1	Pb^{4+} titration[5]
2-Mercaptopropionic acid	96.4	96.6	ICl titration[6]
p-Toluenethiol	98.5	98.4	Co^{3+} titration[7]
2-Diethylaminoethanethiol HCl	98.1	98.2	Chloramine-T[8]
1-Propanethiol	94.8	94.5	Cu^{2+} titration[9]
Toluene-α-thiol	98.5	98.2	Acetylation[10]
Mercaptoacetic acid	80.0	80.3	Periodate titration[11]
Thiobenzoic acid	95.3	95.0	Alkalimetry[12]
2-Mercaptobenzothiazole	98 0	97.8	NBS titration[13]
1-Butanethiol	90.3	90.6	PIA titration[14]
2-Mercaptoethanol	99.5	99.3	Cu^{2+} titration[15]
Allylthiol	93.4	93.2	Acetylation[10]
p-Chlorotoluene-α-thiol	98.4	98.7	Iodimetry[3]
2-Butanethiol	97.2	97.4	NBB titration[16]
2-Mercaptoethylammonium chloride	97.4	97.5	OIB titration[17]
1-Pentanethiol	88 2	88.4	Hg^{2+} titration[18]
Methyl 3-mercaptopropionate	96.2	96.0	Iodimetry[3]
Benzenethiol	98.7	99.0	Nitrite titration[19]
2 Naphthalenethiol	99.3	99.1	Cu^{2+} titration[20]
Toluenethiol (mixed isomers)	93.2	93.0	Alkalimetry[12]
m-Mercaptobenzoic acid	99.5	99.7	Iodimetry[3]
m-Chlorothiophenol	98.8	99.0	PIA titration[14]
o-Toluenethiol	98.1	98.3	Iodimetry[3]
o-Chlorobenzenethiol	99.6	99.8	Pb^{4+} titration[5]
Glycerol-1-thiol	79.2	79.0	Ferricyanide reaction[21]
Cyclohexanethiol	95.3	95.7	Cu^{2+} titration[20]

a, Mean of 10 determinations ; relative standard deviation in the range 0.1-0.3%.

TABLE—2 DETERMINATION OF THIOUREAS WITH *o*-DIACETOXY IODOBENZOATE

Sample	Purity, %		
	Present Method[a]		Comparison method
Thiourea	99.7	99.9	Hypoiodite[22]
Thiosemicarbazide	99.3	99.6	Nitrite titration[23]
Phenylthiourea	99.7	100.1	Bromimetry[24]
o-Tolylthiourea	96.8	97.2	Chloramine-T[25]
p-Tolylthiourea	98.2	98.5	Iodine monochloride[26]
Allylthiourea	96.6	96.1	Sulphur analysis
p-Bromophenylthiourea	95.6	96.0	Iodine monochloride[26]
m-Chlorophenylthiourea	98.2	97.9	Bromimetry[24]
p-Anisylthiourea	99.9	100.4	Iodine trichloride[27]
m-Anisylthiourea	97.0	97.4	Iodine monochloride[26]
n-Butylthiourea	98.7	99.0	Cerimetry[28]
n-Amylthiourea	99.6	99.2	Cerimetry[28]
o-Ethoxyphenylthiourea	98.4	98.2	Chloramine-T[25]
p-Tolylthiourea	98.0	97.4	Pb^{4+} titration[29]
Methylthiourea	98.2	98.1	Nonaqueous cerimetry[30]

a Average of 10 determinations; relative standard deviation in the range 0.2-0.5%

and disulphide are given in Tables 3-5. In Table 6, results are given for the determination of disulphides formed by titration of mercaptan solution with *o*-diacetoxy iodobenzoate. As a check, sulphides and disulphides were determined by the method of Siggia[8] and by total sulphur analysis (Tables 3 & 4).

TABLE—3 DETERMINATION OF SULPHIDE WITH *o*-DIACETOXY IODOBENZOATE

Sample	Purity, %		
	Present Method		Comparison method
Dibenzylsulphide	98.9	99.3	Total sulphur analysis
Methyl *n*-propylsulphide	95.4	96.1	Bromimetry[8]
Methionine	99.5	100.1	PIA titration[31]
Di *n*-butylsulphide	99.8	99.5	Bromimetry[8]

TABLE—4 DETERMINATION OF DISULPHIDES WITH *o*-DIACETOXY IODOBENZOATE

Sample	Purity, %	
	Present Method	Bromimetry[8]
Cystine	99.0	99.3
Di *n*-butyldisulphide	97.3	96.9
Di *n*-benzyldisulphide	99.7	100.2
Di *n*-pentyldisulphide	98.4	98.1
Di *n*-propyldisulphide	94.7	94.6
Diphenyldisulphide	95.3	95.7

TABLE—5 DETERMINATION OF CRUDE SAMPLES

	Purity, %	
	Present Method	Total sulphur analysis
Dibenzylsulphide	87.6	88.3
Di *n*-butylsulphide	79.7	81.1
Dibenzyldisulphide	84.3	84.4

Purity of crude samples were determined by total sulphur analysis (Table 5). Table 7 summarizes the results for the determination of organic derivatives of dithiocarbonic acid and carbon disulphide. The time allowed for complete reaction in this case should not be increased as dixanthogens also get oxidized slowly by an excess of *o*-diacetoxy iodobenzoate. In Table 8, results are given for the determination of mercaptans and derivatives of dithiocarbonic acid in the presence of foreign substances. The substances chosen to study the effect, include compounds that interfere in other methods and compounds that contain other sulphur functions. In the determination of thioureas large amounts of glycine,

TABLE—6 DETERMINATION OF DISULPHIDES FORMED IN COMPLETELY TITRATED MERCAPTAN SOLUTION

	mole		
	RSH Titrated	RSSR Formed	RSSR Recovery[a] (%)
Mercaptoacetic acid	0.582	0.289	99.3
1-Butanethiol	0.759	0.380	100.3
1-Pentanethiol	0.286	0.142	99.8
2-Mercaptopropionic acid	1.163	0.578	99.2
Benzenethiol	1.029	0.516	100.3
Toluene-α-thiol	0.874	0.431	98.5

a % recovery takes into account theoretically calculated value.

TABLE—7 DETERMINATION OF CARBON-DISULPHIDE AND ORGANIC DERIVATIVES OF DITHIOCARBONIC ACID BY *o*-DIACETOXY IODOBENZOATE

Sample	Purity, %		
	Present Method[a]	Iodine titration[32-34]	Sulphur Analysis
K Methylxanthate	96.5	96.9	97.6
Na Ethylxanthate	89.4	90.1	89.8
K *n*-Propylxanthate	99.6	99.8	99.9
K *n*-Butylxanthate	94.1	93.9	94.5
K *iso*-Propylxanthate	78.6	79.1	78.8
K *iso*-Butylxanthate	92.3	92.9	92.6
K Amylxanthate	96.8	97.1	97.5
K *iso*-Amylxanthate	94.7	94.4	95.0
K Allylxanthate	93.9	94.3	95.3
K Cyclohexylxanthate	75.7	76.2	76.1
K *sec*-Butylxanthate	98.9	99.1	99.6
Carbon disulphide	95.2	94.8	—

a Average of 10 determinations; relative standard deviation in the range 0.3-0.5%.

TABLE—8 DETERMINATION OF MERCAPTANS, AND XANTHATES IN PRESENCE OF FOREIGN SUBSTANCES

Sample determined	Substance added	Molar ratio, added subs/ sample	Recovery[a], (%)
Mercaptopropionic acid	Potassium cyanide	83 : 1	100.7
	Dimethylsulphoxide	314 : 1	100.0
	Diethylsulphide	14 : 1	100.0
K *n*-Butylxanthate	Acrylonitrile	60 : 1	99.7
	Diacetonealcohol	7 : 1	100.2
	Dimethylsulphoxide	38 : 1	99.0
	Acetone	9 : 1	99.9
2-Mercaptoethanol	Thiophene	10 : 1	100.5
	Dibenzyldisulphide	70 : 1	100.0
	Alanine	69 : 1	100.1
	Formic acid	90 : 1	100.5
K Allylxanthate	Carbon disulphide	58 : 1	101.2
	Cystine	27 : 1	100.1
	Glycine	34 : 1	100.0
	Alanine	44 : 1	100.0
	Thiophene	19 : 1	101.8
2-Mercaptopropionic acid	Dextrose	170 : 1	100.2
	Carbon disulphide	105 : 1	100.2
	Methylacrylate	10 : 1	101.0
	Acrylonitrile	94 : 1	99.7

a Average of 4 determinations ; % recovery takes into account previously determinated purity of sample (Table 3).

alanine, formic acid, dextrose and urea do not interfere but organic sulphides and disulphides interfere. In the determination of sulphides and disulphides, alanine, glycine, dextrose, fumaric, cinnamic and formic acids can be tolerated.

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Studies on Hydroxamic Acids : Solvent Extraction of Metal Ions with N-p-chlorophenyl-2-thenohydroxamic Acid

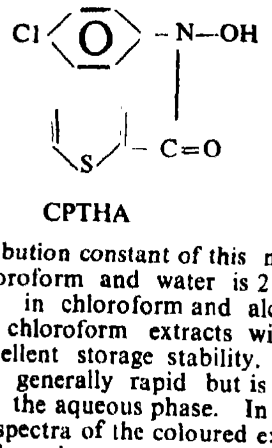
RAMA PANDE AND S. G. TANDON

Department of Chemistry, R. S. University, Raipur-492002

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The solvent extraction of several metal ions with N-*p*-chlorophenyl-2-thenohydroxamic acid is investigated qualitatively. The coloured chloroform extractable complexes of Ce(IV), Cu(II), Fe(II, III), Ti(IV), U(VI), V(V) and Zr(IV) are attractively suited for further examination for colorimetric determination and solvent separation.

N-PHENYLBENZOHYDROXAMIC acid[1-6] and its analogues[7,8] are now widely used for solvent separation and colorimetric determination of metal ions. In the present communication the solvent extraction studies with N-*p*-chlorophenyl-2-thenohydroxamic acid, trivial name CPTHA[9], with metal ions are briefly described.



CPTHA

The distribution constant of this new compound between chloroform and water is 215 ± 5 at 25°. Its solutions in chloroform and alcohol are very stable. The chloroform extracts with metal ions too have excellent storage stability. Extraction of metal ions is generally rapid but is dependent on the acidity of the aqueous phase. In figures 1 and 2 the typical spectra of the coloured extracts in near UV and visible regions are presented. The spectral characteristics of these extracts and conditions of reactions are given in Table 1. It is observed that

TABLE—1 SPECTRAL CHARACTERISTICS OF COLOURED CPTHA METAL ION EXTRACTS IN CHLOROFORM

Metal Ion	Aqueous Phase, *p*H	Colour of Extract	Wavelength of absorption maximum, nm
Ce^{+4}	8*N* HCl	Yellow	GA
Ce^{4+}	1-2	Yellow	365
Cu^{2+}	1-2	Yellow	GA
Fe^{2+}	2-4	Red	445
Fe^{3+}	2-4	Red	445
Ti^{4+}	8*N* HCl	Yellow	348
UO^{2+}	2-4	Yellow	GA
VO_3^-	2-10*N* HCl	Violet	530
VO_3^-	0-1 *N* HCl	Brown	465
Zr^{4+}	2-3	Yellow	375

GA = General Absorption.

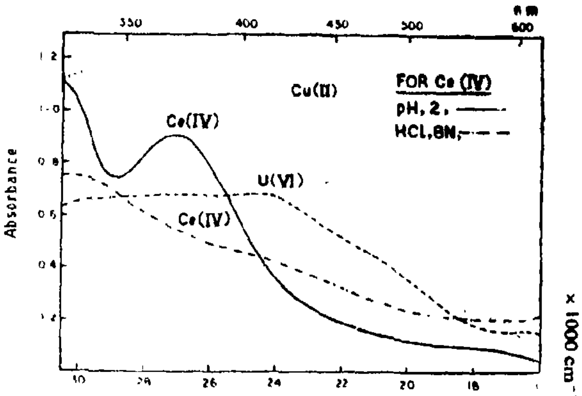


Fig 1 Absorption spectra of CPTHA extracts in chloroform

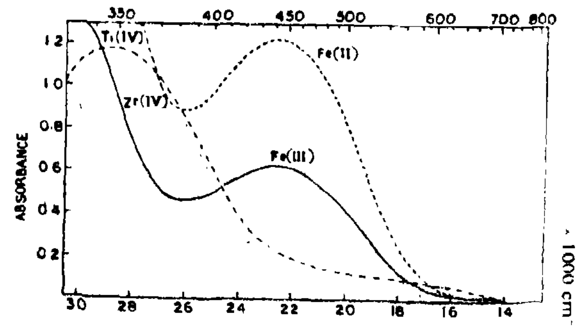


FIG 2. ABSORPTION SPECTRA OF CPTHA EXTRACTS IN CHLOROFORM

CPTHA is a versatile extractive reagent. Of the many metal ions which give coloured extracts with CPTHA in chloroform Ce(IV), Fe (II, III), Ti(IV), V(V) and Zr(IV) only show well defined absorption band. Cu(II) and UO_2^{2+} exhibit general absorption. Ce(IV) gives yellow extracts both from weakly and strongly acidic solutions but the stoichiometric compositition of complexes seem to be different. For example, its yellow extract at *p*H 2 gives a broad band at 365 nm where as the extract obtained from 8N hydrochloric acid shows general absorption only. A number of common metal ions such as Al(III), Mn(II),

Pb(II) and others gave colourless extracts. Rare earth ions gave both coloured and colourless extracts but their extraction was very sensitive to *p*H of the aqueous phase; these were partially extracted even on long periods of shaking with concentrated solutions of CPTHA. The coloured extracts are attractively suited for detailed investigation for colorimetric applications. These and their extraction parameters in various other water-immiscible solvents are being further investigated. The colourless extracts are not likely to be useful for direct quantitative determination of metal ions although these may find applications in solvent separations.

Experimental

Apparatus :

The spectra of coloured metal hydroxamates were recorded on SPECORD, Carl Zeiss, Jena ultraviolet-visible recording spectrophotometer equipped with matched quartz cells of 10 mm path length. Narrow range and wide range indicator papers were used for rapid and approximate measurement of *p*H. Accurate measurement of *p*H was made on Systronics *p*H meter.

Solutions of Diverse Ions :

The solutions of various ions were prepared from A.R, grade salts following the procedure of West [10]. The concentration of the desired ion was generally 20 mg. per ml.

Reagent Solution :

A 0.1% solution of CPTHA in ethyl alcohol free chloroform was used for all extraction work.

Buffer Solutions :

10% w/v. aqueous solutions of sodium and ammonium acetates and ammonium chloride were used as buffer.

General Procedure for Solvent Extraction of CPTHA with Metal Ions :

In a short-stemmed pear shaped separatory funnel 5 to 10 ml solution, containing 2 to 5 mg of the metal ion to be tested, was taken and the acidity was adjusted to a desired value by the addition of acid, alkali or buffer solution. The solution was shaken vigorously with 5 to 10 ml of the reagent solution in chloroform for about 5 minutes or longer. The organic layer was then separated, dried over anhydrous sodium sulphate and tested, whenever necessary, for extraction of metal ion by suitable spot tests. The absorption spectra of coloured metal extracts were recorded after suitable dilution.

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Study of Beans of *Pithecolobium saman* Benth

I. P. VARSHNEY and PRAMOD VYAS

Department of Chemistry, G. S. Institute of Technology and Science, Indore-452 003

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Pithecolobium saman **Benth beans yielded free sucrose and a new saponin named as Samanin B which is a glycoside of Acacic acid with glucose, arabinose, xylose and rhamnose in molar ratio of 4 : 2 : 1 : 1.**

P*ITHECOLOBIUM saman* commonly known as 'Raintree' is a member of family Leguminoseae, sub-family Mimoseae. Nigam *et al*[1] reported a number of compounds viz. hexacosanol, octacosanol, octacosonoic acid, β-D-glucoside of ⍺-spinasterol, ⍺-spinasterone, hentricotane, lupeonone, lupeol, palmetic acid and stearic acid and a mixture of flavonoids including kaempferol in various parts of the plant and did not encounter any saponin in any part. The presence of saponin was reported in the bark by earlier workers[2]. The leaves have been reported to contain alkaloids[3,4].

Varshney *et al*[5] have studied the saponin samanin A of the seeds and found it to be a glycoside of acacic acid with 15 moles of four sugars.

The present investigation deals with the study of the saponin and free sugars of the beans without seeds, from which saponin and sucrose was isolated in good quantities.

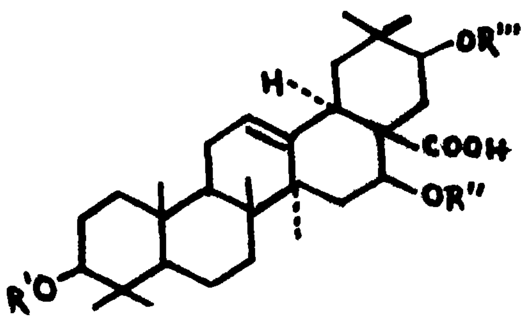
The purity of saponin a colourless product, m.p. 194-196° $[\alpha]_D = -74$ (C-0.98 MeOH) was tested by TLC and electrophoresis, and has been named as Samanin B. It formed an acetate, m.p. 150-152° $[\alpha]_D = -54$ (C-1%$CHCl_3$) samanin B on acid hydrolysis with sulphuric acid in usual manner[6] gave an acid genin (25%) identified as acacic acid (3 β, 16 β, 21 β, trihydroxy, olean-12-ene-18-⍺-H, 28 oic acid). Acid genin on acetylation gave acacic acid diacetyl lactone[7]. The fractions 26-35 gave crystalline compound which has been identified as sucrose.

The sugars obtained by hydrolysis of samanin B on paper chromatography in butanol : pyridine : water (6 : 4 : 3) showed the presence of four sugars identified as glucose, arabinose, xylose and rhamnose by co-chromatography with authentic samples. The sugars were then separated by preparative paper chromatography and were separately estimated by photocolorimetric method[8] and the molar ratio of glucose, arabinose, xylose and rhamnose was found to be 4 : 2 : 1 : 1.

Samanin B on alkaline hydrolysis with methanolic potassium hydroxide did not give any sugar and the saponin was recovered unchanged indicating the absence of ester linkage in Samanin B i.e. there are no sugars attached at C-28 COOH group.

The infra-red spectra of samanin B and its acetate did not show any lactonisation on acetylation, between 21 hydroxyl and 28 carboxylic groups as is the case of acacic acid[7]. This indicated that 21 hydroxyl group is not free in the samanin B and all the sugars are attached at all the three hydroxyl groups or any of them (C-3OH, C-16 OH, C-21 OH). All attempts to knock out the sugars selectively failed.

On the basis of the above observations, samanin B, is concluded to be a glycoside of acacic acid (3 β, 16 β, 21 β, trihydroxy-olean-12-ene, 18 ⍺-H, 28 oic acid) with glucose, arabinose, xylose and rhamnose present in molar ratio of 4 : 2 : 1 : 1 attached at C-3, C-16 and C-21 hydroxyl groups.



R' + R'' + R''' = Glucose : Arabenose. Xylose : Rhamnose (4 : 2 : 1 : 1)

Fig 1

Experimental

Isolation of Sucrose and Samanin B :

The beans (500 gms) were broken and after the removal of seeds, defatted with petroleum ether (60-80°). Removal of petroleum ether yielded a dark yellow green oily substance (5.5 gms). The well defatted pieces of beans were exhaustively extracted with ethanol. Ethanolic extract was concentrated and left for several days, it gave a colourless crystalline substance m.p. 186° which has been identified as sucrose by mixed m.p. and paper chromatography with authentic sample. The filtrate was then evapoated under reduced pressure to yield a brown syrupy mass which was successively extracted with petroleum ether, ether chloroform, carbon tetrachloride and acetone[6]. The residue was dissolved in minimum quantity of methanol and precipitated by adding to a large amount of acetone/ether, to yield a light brown powder (30 gms). On TLC it showed two spots. The mixture was further purified by chromatography on column of silica gel using butanol : methanol : water (10 : 4 : 14) as eluant fractions 920 gave pure saponin, Samanin B as colourless powder. m.p. 194-196°. The purity of the saponin was confirmed by two dimensional thin layer chromatography and by electrophoresis (300 volts, borate buffer).

Acetylation of Samanin B :

Samanin B (50 mg) was suspended in pyridine (5 ml) and acetic anhydride (5 ml) was added to it. The mixture was kept over night. It was then poured over ice/water with constant stirring. After standing for half an hour it was filtered and dried. It was dissolved in chloroform and precipitated by adding dropwise to petroleum ether. It gave colourless substance, m.p. 150-152° $[\alpha]_D = -54$ (C. 1°/o $CHCl_3$).

Acid hydrolysis of Saponin :

Saponin (200 mg) was dissolved in 100 ml of water and sulphuric acid was added to make 10%, it was heated on water bath for an hour and then refluxed for 4 hr. Sapogenin which separated was filtered, washed free of acid and dried (58 mg).

Purification of the genin :

The genin (50 mg) was dissolved in 5% methanolic potassium hydroxide and refluxed for 2 hr. on water bath. Thereafter half of the methanol was evaporated and the contents were diluted with water and extracted a number of times with ether. Aqueous solution left was acidified with hydrochloric acid which precipitated genin. In was filtered, washed and dried. It was crystallised from methanol and had m.p. 275-282°. The genin was identified as acacic acid by m.p., m.m.p. and TLC with authentic sample of acacic acid. Acetate, m.p. 235-236° crystallised from methanol, was identified with acacic acid acetate by, direct comparison with the authentic samples.

Identification of sugars :

Hydrolysate obtained by acid hydrolysis of Samanin B was neutralised with freshly precipitated barium carbonate and then deionised by passing through the columns of ion-exchange resins (Amberlite IRA 400 and Amberlite IR 120 (H^+). The neutral sugar solution thus obtained was evaporated under reduced pressure to yield a light brown syrup. It was then chromatographed on Whatman filter paper No-1 alongside with authentic samples of sugars, this showed the presence of 4 sugars identified as glucose, arabinose, xylose and rhamnose.

Separation and estimation of sugars :

The sugar mixture was applied as a narrow streak on Whatman filter paper No. 3MM. After running the paper for 60 hr. in butanol : pyridine : water (6 : 4 : 3) the strips were cut by the aid of guide strips. Extraction of strips separately with 50% methanol and evaporation gave four different sugars, the purity of which was tested again by paper chromatography. The sugars were then estimated as glucose by photocolorimetric method using phenol sulphuric acid[8]. This gave the molar ratio of glucose, arabinose, xylose and rhamnose as 4 : 2 : 1 : 1.

Alkaline hydrolysis of saponin :

Saponin (50 mg) was dissolved in 50 ml. of methanol and to it aqueous sodium hydroxide solution (50 ml, 5%) was added and then refluxed for 4 hr. on water bath. The methanol was slowly evaporated adding water to make up the constant volume and then neutralised with hydrochloric acid. This was then extracted with *n*-butanol. The butanol extract on evaporation to dryness under reduced pressure and paper chromatography did not reveal the presence of any sugar. On TLC, it did not show any change in mobility from the mobility of the starting material, i.e. Samanin B.

Free Sugars :

The fraction (26-36) from column chromatography gave a crystalline product which has been identified as free sucrose by m.p., m.m.p. and paper chromatography with authentic sample of sucrose.

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Thanks are due to the authorities of G.S. Institute of Technology and Science, Indore for facilities.

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Solid State Interaction Between Zinc Phosphate and Urea Nitrate

T. K. MUKHERJEE* and D. N. PATHAK

Department of Chemistry, Regional Institute of Technology, Jamshedpur

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Zinc phosphate reacts with urea nitrate when the powders of the two solids are ground together for 1-2 hours. The resulting product becomes completely water soluble when the mole ratio of tribasic zinc phosphate to urea nitrate is 1:4 and may be utilized as a suitable fertilizer for nitrogen, phosphorus and zinc deficient soils. The interaction occurs in two steps : (i) formation of $ZnHPO_4$ in the solid phase and (ii) conversion of $ZnHPO_4$ to $Zn(H_2PO_4)_2$ in the solid-liquid phase.

AMONG different micronutrients, zinc deficiencies are more wide spread in the Indo-Gangetic plains of Punjab, Haryana and Uttar Pradesh*. It has been reported by a large number of workers[1,2,4,7] that heavier doses of phosphatic fertilizers induce deficiency and unavailability of zinc to plants. In the present investigation an attempt has therfore been made to explore the conditions for the manufacture of a mixed fertilizer suitable to supply zinc in presence of phosphorus in the zinc deficient soils, on the lines recently reported by Pant and Pathak[5]. The work consists of grinding varying amounts of urea nitrate with a fixed amount of tribasic zinc phosphate. The ratio of urea nitrate to zinc phosphate which makes the resulting product completely water soluble has been investigated.

Experimental

All the chemicals used were BDH AnalaR grade.

A series of mixtures were prepared by mixing 1g mole of zinc phosphate, $Zn_3(PO_4)_2 4H_2O$ with varying amounts of urea nitrate and each mixture was ground in an agate mortar for 1-2 hours under dry conditions.

Water soluble and citrate soluble phosphates in the ground mixtures were determined by methods reported in an earlier communication[6]. Phosphorus was estimated volumetrically after precipitating with molybdate solution and zinc was estimated gravimetrically as zinc pyrophosphate*.

The amount of zinc nitrate formed in the ground mixture was estimated by leaching with absolute alcohol in a soxhlet extractor. Since zinc phosphate is insoluble in ethanol the amount of zinc present in the solvent is originating from the zinc nitrate formed.

Discussion

The experimental results (Table 1) indicate that with increasing urea nitate content, the percentage of water soluble phosphate gradually increases, finally resulting in cent per cent water soluble mixtures.

Unprotonated zinc phosphate may react with urea nitrate either when the two reactants are mixed or when the mixture is placed in water. 'In the former case, zinc nitrate is one of the products and is

TABLE 1. WATER AND CITRATE SOLUBLE P_2O_5 IN ZINC PHOSPHATE-UREA NITRATE MIXTURE.

Zinc phosphate to urea nitrate mole ratio	Total P_2O_5 %	Water soluble P_2O_5 %	Citrate soluble P_2O_5 %	Fraction of water soluble P_2O_5 %	Fraction of citrate soluble P_2O_5 %
1 : 0	30.99	—	—	—	—
1 : 1.00	24.43	8.28	7.92	33.48	32.41
1 : 1.50	22.06	10.78	4.47	48 86	20.26
1 : 2.00	20.01	11.05	3.73	55.22	18.64
1 : 2.50	18.47	12.60	3.12	68.21	16.89
1 : 3.00	17.16	14.64	2.72	85.31	15.85
1 : 3.25	16.60	15.32	1.03	92.89	6.20
1 : 3.50	15.98	15.19	0.41	95.07	2.58
1 : 3.75	15.44	15.26	—	98.77	—
1 : 4.00	14.94	14.93	—	99.98	—

*Lecturer in Chemistry, Women's College, Jamshedpur.

soluble in solvents other than water. Hence absolute alcohol is used as the extracting medium. Zinc could be detected in solution, while no phosphate was found in the alcohol. Urea as well as urea nitrate is soluble in the alcohol and only zinc phosphate is left behind as the residue. The zinc nitrate formed in the ground mixture of tri zinc phosphate and urea nitrate is estimated and results are given in Table 2. The zinc nitrate content increases with increasing amount of urea nitrate and

TABLE 2. ZINC NITRATE CONTENT IN ETHANOL EXTRACT [ZINC PHOSPHATE (9.1622 g)+UREA NITRATE]

Wt. of urea nitrate (g)	Zinc phosphate to urea nitrate mole ratio	No. of g atoms of zinc soluble in alcohol per mole of zinc phosphate
1.23	1 : 0.50	0.1560
2.46	1 : 1.00	0.4010
3.69	1 : 1.50	0.8160
4.92	1 : 2.00	1.2800
5.53	1 : 2.25	1.2780
6.15	1 : 2.50	1.2420
7.38	1 : 3.00	1.2620

reaches a limiting value when the mole ratio of zinc phosphate to urea nitrate is 1 : 2. Further increase in the urea nitrate content does not give rise to increased amount of zinc nitrate in the extract. The limiting value of zinc nitrate found corresponds to one mole for every mole of tri zinc phosphate mixed with two moles of urea nitrate.

It is clear from the above observation that the interaction between urea nitrate and unprotonated zinc phosphate occurs in the following two steps :

$$Zn_3(PO_4)_2 + 2CO(NH_2)_2HNO_3 = 2ZnHPO_4 + 2CO(NH_2)_2 + Zn(NO_3)_2 \quad \ldots \quad (i)$$

$$2ZnHPO_4 + 2CO(NH_2)_2HNO_3 = Zn(H_2PO_4)_2 + 2CO(NH_2)_2 + Zn(NO_3)_2 \quad \ldots \quad (ii)$$

The first step is a solid phase reaction whereas the second step is a solid-liquid phase reaction in which the nitric acid formed by the dissociation of urea nitrate reacts with dibasic zinc phosphate produced in the first step. This is further supported by the fact that at the later stage of grinding the powders form a paste.

It is well known that when an excess amount of tribasic phosphate reacts with less amount of an aqueous acid, a mixture of dibasic phosphate and monobasic phosphosphate is obtained. But the protonation of zinc phosphate by urea nitrate follows a path other than that expected in an aqueous medium. This is supported by the fact that $Zn(H_2PO_4)_2$ is not produced in step (i). Had it been one of the products the side reaction :

$$Zn(H_2PO_4)_2 + CO(NH_2)_2 = ZnHPO_4 + CO(NH_2)_2 . H_3PO_4$$

would occur and urea phosphate, $CO(NH_2)_2.H_3PO_4$ soluble in absolute alcohol would have been the resulting product. Since no alcohol soluble phosphate is detected in the ground mixture of urea nitrate and zinc phosphate the possibility of formation of $Zn(H_2PO_4)$ in the (i) step is completely ruled out. Hence it is concluded that $ZnHPO_4$ formed in the (i) step dissolves in excess urea nitrate solution to form $Zn(H_2PO_4)_2$ in the (ii) step, rendering the whole mixture water soluble.

The experimental results clearly indicate that a ground mixture of tribasic zinc phosphate and urea nitrate in the mole ratio of 1 : 4 is a good source of nitrogen, phosphorus and zinc to plants and therefore may be utilized as a suitable fertilizer for the nutrient deficient soils of different parts of India.

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Notes

Kinetics of the Oxidation of Neutralized β-Phenyl Pyruvic Acid by Alkaline Hexacyanoferrate(III)

KALYAN K. SEN GUPTA*, HRIDAY R. CHATTERJEE and SHIPRA SEN GUPTA

Department of Chemistry, Jadavpur University, Calcutta-700032.

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THE oxidation mechanisms involving α-ketoacids and various ions of transition metals[1-4] along with the halogenation reactions of α-keto acids[5-6] have already been studied. The kinetics of the oxidation of some α-keto acids by alkaline hexacyanoferrate(III) have been reported in our earlier communications[7-8]. Oxidation of β-phenyl pyruvate ion has been studied in view of the interesting results obtained with glyoxylate and pyruvate ions.

Experimental

Reagents : Neutralized β-phenyl pyruvic acid (Fluka A.G.) was used. The details of other reagents have been mentioned in earlier communications[7,8].

Procedure : The rate of disappearance of hexacyanoferrate(III) was followed spectrophotometrically[7]. The reaction was initiated by adding requisite quantity of the substrate into the solution containing the oxidant and alkali (in uncatalyzed reaction) or the oxidant, carbonate-bicarbonate buffer and osmium(VIII) (in catalyzed reaction), all maintained at a constant temperature. The disappearance of oxidant follows first order kinetics in the case of the uncatalyzed reaction and zero order kinetics in the case of the catalyzed reactions. The rate of loss of oxidant was followed for at least 50% reduction of initial hexacyanoferrate(III). All experiments were performed at 33° and osmium (VIII) catalyzed oxidations were always carried out at osmium(VIII) concentration of $2.0 \times 10^{-6} M$ unless otherwise mentioned.

The equivalents of heracynaferrate(III) ion consumed per mole of substrate were 6.5 in both the cases of uncatalyzed and catalyzed oxidations. The products of oxidation were found to be a mixture of benzaldehyde and benzoic acid in both the cases. Benzaldehyde was identified by preparing its 2 : 4 D.N.P. derivative (m.p.=234-235°, lit m.p.[9]=235°). The melting point of benzoic acid, after separation, was noted to be 121° (lit m.p [9]=121°).

* To whom all correspondence to be made.

Results and Discussion

In some experiments the concentrations of the reducing substrate, hydroxyl ion and catalyst (where present) were kept constant but the concentrations of initial oxidant were varied. The average values of k_1 (k_1=pseudo first order rate constant) are $(3.75 \pm 0.07) \times 10^{-4}$ (sec^{-1}) at [Hexacyanoferrate(III)] $=(1.0\text{-}7.0) \times 10^{-4}$M, [β-phenyl pyruvate]= 2.18×10^{-3}M and $[OH^-]=1.0 \times 10^{-2}$M whereas the values of k_0 (k_0=zero order rate constant) for the catalyzed reaction are $(3.7 \pm 0.1) \times 10^{-8}$ (mole lit^{-1} sec^{-1}) at [Hexacyanoferrate(III)]=(1.95-5.0) × 10^{-4}M, [β-phenyl pyruvate]=2.18×10^{-3}M and $O[H^-]=6.3 \times 10^{-6}$M. The values of k_1 and k_0 along

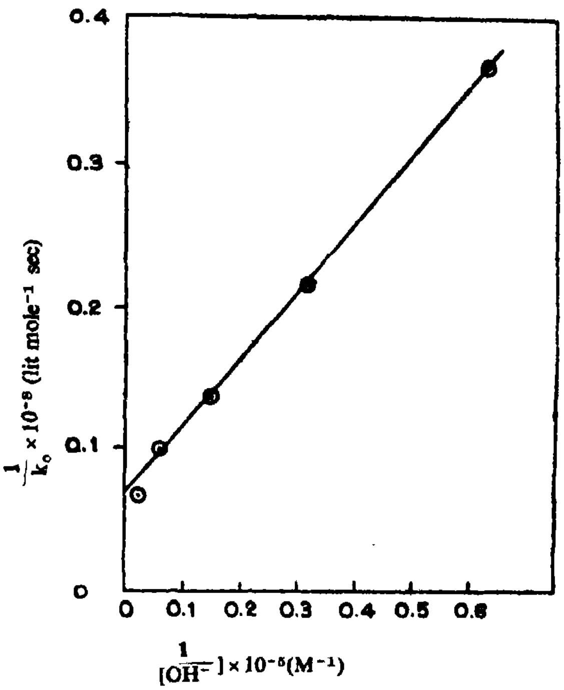


FIGURE 1 : Plot of $\frac{1}{k_0}$ against $\frac{1}{[OH^-]}$ for the osmium (VIII) catalyzed oxidation.

with the quotients, k_1/ [β-phenyl pyruvate] and k_0/[β-phenyl pyruvate] for the respective reactions are summarized in Table 1. The rates are found to be proportional to the initial concentration of the reducing substrate.

The effect of hydroxyl ion concentration on the initial rates was studied at constant reactants and

catalyst (where present) concentrations (Table 2).

TABLE-1 EFFECT OF VARYING [β-PHENYL PYRUVATE] ON K_1 AND K_0 OF UNCATALYZED AND CATALYZED REACTIONS RESPECTIVELY.

(a) $[Fe(CN)_6^{3-}] = 5.0 \times 10^{-4}$M, $[OH^-] = 0.75 \times 10^{-2}$M
(b) $[Fe(CN)_6^{3-}] = 2.92 \times 10^{-4}$M, $[OH^-] = 6.3 \times 10^{-5}$M.

	[β-phenyl pyruvate] $\times 10^3$(M)	2.18	4.36	6.54	8.72	10.0
(a)	$k_1 \times 10^4$(sec^{-1})	2.76	4.98	7.67	10.5	12.5
	$\frac{k_1}{[\beta\text{-phenyl pyruvate}]} \times 10$ (lit mole^{-1} sec^{-1})	1.27	1.14	1.17	1.20	1.25
	[β-phenyl pyruvate] $\times 10^3$(M)	2.18	4.36	6.54	8.72	10.9
(b)	$k_0 \times 10^8$(mole lit^{-1}sec^{-1})	3.88	7.31	11.5	14.6	18.2
	$\frac{k_0}{[\beta\text{-phenyl pyruvate}]} \times 10^5$(sec^{-1})	1.78	1.68	1.76	1.67	1.67

TABLE-2 EFFECT OF HYDROXYL ION ON THE PSEUDO FIRST ORDER RATE CONSTANT OF UNCATALYZED REACTION.

$[Fe(CN)_6^{3-}] = 5.0 \times 10^{-4}$M, [β-phenyl pyruvate] $= 2.18 \times 10^{-3}$M

$[OH^-] \times 10^2$(M)	0.5	1.0	1.5	2.0	2.5
$k_1 \times 10^4$(sec)$^{-1}$	1.79	3.65	5.84	7.36	8.33
$\frac{k_1}{[OH^-]} \times 10^2$(lit mol^{-1}sec^{-1})	3.58	3.65	3.89	3.68	3.33

The values of $k_1/[OH^-]$ in the uncatayzed reaction indicate that the rate is directly proportional to the initial OH^- concentration, whereas in the latter case the values of $k_0/[OH^-]$ gradually decreases with the increase in $[OH^-]$ and the plot of $1/k_0$ against $1/[OH^-]$ is linear making an intercept (Figure 1). The reaction is too slow to be studied in hydroxyl ion concentration of 10^{-5}M. At this lower concentration of alkali, the reaction takes place at measurable rate only in the presence of catalyst. It seems that the rate is directly proportional to osmium(VIII) concentrations upto $[Os(VIII)] \leqslant 3.0 \times 10^{-6}$M and after that the increase in rate is not significant and has tendency to remain constant (Figure 2).

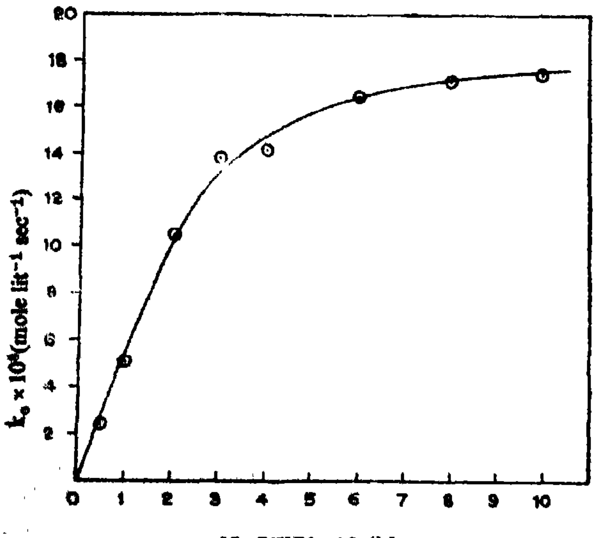


FIGURE 2: Plot of k_0 against [Osmium (VIII)].

The values of k_2 ($k_2 = k_1/[\beta$-phenyl pyruvate]) and k_1 ($k_1 = k_0/[\beta$-phenyl pyruvate]) for uncatalyzed and catalyzed oxidations respectively have been calculated at various temperatures. The values of k_2 have been calculated to be 2.20×10^{-2}, 3.8×10^{-2}, 7.0×10^{-2} and 17.6×10^{-2} (lit mole^{-1} sec^{-1}) at 31.5, 36.0, 40.0 and 45.0° respectively whereas the values of k_1 have been found to be 1.6×10^{-5}, 2.80×10^{-5} and 4.05×10^{-5} (sec^{-1}) at 33, 40.9 and 45.8° respectively for the catalyzed reaction. The values of $\Delta H^{\neq}$ have been found to be 30.0±3.5 and 13.3±1.2 (k cal mole^{-1}) for the uncatalyzed and catalyzed reactions respectively. The corresponding values of $\Delta S^{\neq}$ are 31.9±9.5 and −37.2±3.0 (e.u.) respectively.

It is suggested that β-phenyl pyruvate (S) combines reversibly with the oxidant to form a complex(X) which in turn reacts with hydroxyl ion to give a free radical (Y) and hexacyanoferrate(II). The reaction mixture gave a suspension on addition of acrylamide. The free radical further picks up hexacyanoferrate(III) to give initial products (P*) of oxidation.

Scheme I

$$S + Fe(CN)_6^{3-} \underset{k_{-1}}{\overset{k_1'}{\rightleftharpoons}} X \quad \dots \quad (1)$$

$$X + OH^- \xrightarrow{k_2} Y + Fe(CN)_6^{4-} \quad \dots \quad (2)$$

$$Y + Fe(CN)_6^{3-} \xrightarrow{k_3} P^* + Fe(CN)_6^{4-} \quad \dots \quad (3)$$

Applying steady state approximation in intermediate X and Y, we get equation (4)

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k'_1 k_2 [S][Fe(CN)_6^{3-}][OH^-]}{k_{-1} + k_2[OH^-]} \quad \dots \quad (4)$$

The first order rate constant k_1 comes out to be

$$k_1 = \frac{2k'_1 k_2 [S][OH^-]}{k_{-1} + k_2[OH^-]} \quad \dots \quad (5)$$

If $k_{-1} \gg k_2[OH^-]$ the equation (5) reduces to equation (6) which is consistent with the experimental findings.

$$k_1 = k[S][OH^-] \quad \dots \quad (6)$$

where, $k = \frac{2k'_1 k_2}{k_{-1}}$

It has earlier been mentioned[10,11] that perosmate anion exists as $HOsO_5^-$. It is likely, therefore, that the complex (X') is formed by the interaction of substrate (S) and $HOsO_5^-$ (designated by Os (VIII). The complex (X') thus formed decomposes in the presence of OH^- to give initial products of oxidation (P*) and osmium (VI). The latter is finally oxidized by two molecules of hexacyanoferrate (III) regenerating osmium (VIII).

Scheme II

$$S + Os(VIII) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X' \quad \ldots \quad (7)$$

$$X' + OH^- \xrightarrow{k_5} P^* + Os(VI) + H_2O \quad \ldots \quad (8)$$

$$2Fe(CN)_6^{3-} + Os(VI) \xrightarrow{k_6} Os(VIII) + 2Fe(CN)_6^{4-} \quad \ldots \quad (9)$$

The rate of formation of the complex is zero at steady state and hence the concentration of complex

$$[X'] = \frac{k_4[S][Os(VIII)]}{k_{-4} + k_5[OH^-]} \quad \ldots \quad (10)$$

The rate of disappearance of hexacyanoferrate (III) is

$$-\frac{d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_4k_5[S][Os(VIII)][OH^-]}{k_{-4} + k_5[OH^-]} \quad \ldots \quad (11)$$

$$1/\left(-\frac{d[Fe(CN)_6^{3-}]}{dt}\right) = \frac{k_{-4}}{2k_4k_5[S][Os(VIII)][OH^-]} + \frac{1}{2k_4[S][Os(VIII)]} \quad \ldots \quad (12)$$

A plot $\frac{1}{\text{reaction velocity}}$ vs. $\frac{1}{[OH^-]}$ should give a straight line with a positive intercept at the Y-axis. Such a plot is shown in Figure 1 which justifies the validity of the rate equation (11). The observed stoichiometry of 6.5 can be explained by considering that steps (i) and (ii) take place to the extent of 80% and 20%respectively. (i)$PhCH_2COCOO^- + 6Fe(CN)_6^{3-} + 5OH^- \rightarrow PhCHO + 2CO_2 + 6Fe(CN)_6^{4-} + 3H_2O$, (ii) $PhCH_2COCOO^- + 8Fe(CN)_6^{3-} + 8OH^- \rightarrow PhCOO^- + 2CO_2 + 8Fe(CN)_6^{4-} + 5H_2O$.

The possibility that enolization of β-phenyl pyruvate followed by the oxidation and subsequent rupture of C–C bond to give initially benzaldehyde and oxalic acid, cannot be totally ruled out. However, it has earlier been shown[9] that oxalic acid is not completely oxidized to CO_2 under the condition at which the reaction is carried out. The absence of oxalic acid in the reaction mixture indicates that oxidation via enolization may not take place.

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Chemical Investigation of *Poecilonearon indicum* Leaves

GOPAL MISRA and S. K. NIGAM, National Botanic Gardens, Lucknow

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POECILONEURON INDICUM Bedd. (N. O. Guttiferae)[1], trade name *Ballagi* is a large tree found in Western Ghats from North Kanara to Travancore at an altitude of 300 – 1,200 m. The tree yields a good quality timber for heavy constructional work. The fruit, bark and root of the plant are reported[2,3] to yield friedelin. As a longe range programme of better utilization of plant resources, investigation with the leaves of *P. indicum* collected from Shimoga forests (Mysore state), has been carried out and the results recorded here.

The alcoholic extractive of the shade dried powdered leaves (2 kg) was successively extracted with *n*-hexane and ether. The hexane extract on keeping deposited an $FeCl_3$ positive dirty yellow powder (9 g) which on crystallisation (pyridine) furnished yellowish crystals, m.p.>350° (Found : C, 55.70 ; H, 2.82, Calcd for $C_{14}H_6O_8$: C, 55.62 ; H, 1.98%) and was identified as *ellagic acid* by positive Griesmeyer Reichelsche reaction, and direct Comparison (TLC, IR) with an authentic sample.

The dark green residue obtained from the filtrate of ellagic acid on subsequent purification was chromatographed over Al_2O_3 column.

The *n*-hexane eluents yielded a substance, m.p. 71° (80 mg) which was identified as *hentriacontane* (m. m.p. ; IR).

The *n*-hexane-benzene (3 : 1) elution of the column gave an LB positive and TNM negative reridue (1.2 g) which on repeated crystallisation from benzene furnished needles, m.p. 256-258° ; $(\alpha)_D^{25}$ – 30° ; ν_{max}^{KBr} 1709 cm^{-1}. It was identified (m.m.p., IR, TLC) as *friedelin* (Found : C, 84.45 ; H, 12.10. Calcd. for $C_{30}H_{50}O$: C, 84.50 ; H, 11.70%).

The *n*-hexane-benzene (1 : 1) elution gave another LB positive and TNM negative residue which on crystallisation from benzene gave needles (700 mg), m.p. 286-288° ; $(\alpha)_D^{25}+29°$; ν_{max}^{KBr} 3484 cm⁻¹ (OH), and was identified (acetate, m.p. 293-295°) as *friedelan-3β-ol*, (m.m.p. TLC, IR). The mother liquor yielded a waxy product (200 mg) which on purification melted at 85-86° ; ν_{max}^{KBr} 3298 (OH), 1459 (CH_2), 732, 722 ($-(CH_2)_n-$) cm⁻¹ and was identified as *hentriacontanol* (lit m.p. 84-85°).

The ethereal extract of the alcoholic extractive (*vide supra*) gave an $FeCl_3$ positive (royal blue ink colour) dark green sticky product which on purification through chromatography (silica gel) and crystallisation (benzene) gave a TLC pure compound (2.5 g) as silky threads, m.p. 145-146° ; ν_{max}^{KBr} 3333 (OH) ; 1701, 1250 (ester) cm⁻¹ (Found : C, 55.45 ; H, 5.25. Calcd. for $C_9H_{10}O_5$: C, 54.54 ; H, 5.05%). It was characterised as *ethyl gallate* (*lit.* m p. 141°) by MS peaks at m/e 198 (M^+), 170 (gallic acid fragment) and triacetate, m.p. 168° (*lit* 170°). It could however, be an artefact of gallic acid which is presumably esterified during alcohol extraction of the plant material.

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Ethyl-N-methylallophanate, a side Product of Reactions in Ethanol with Diazomethane Solution Prepared from Nitrosomethylurea

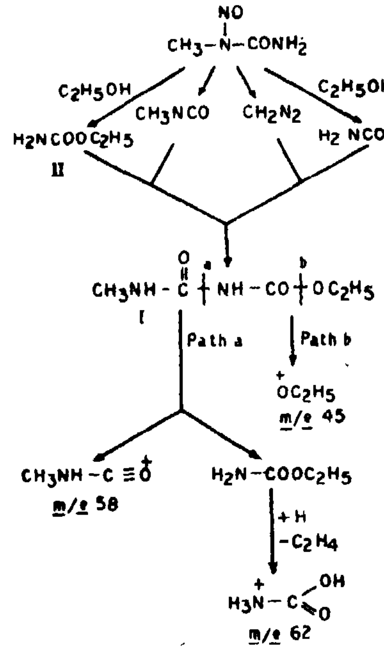
S. C. PAKRASHI and (Mrs.) SUPREETI DATTA

Indian Institute of Experimental Medicine, Calcutta-700032

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WE reported[1] the isolation of compound A, $C_5H_{10}N_2O_3$, m.p. 134° from the acidic fractions of the chloroform extract of the leaves of *Carissa carandas* Linn. It was obtained in the chloroform eluate when the ethanolic mother liquor of ursolic acid was treated with diazomethane prepared from nitrosomethylurea in the standard method[2] and the product was chromatographed over neutral alumina. It has now been established as ethyl-N-methylallophanate (I).

Compound A exhibited a weak UV maximum (ethanol) at 275 nm (ε 27·3) and principal IR (nujol) bands at 3275, 1750, 1657, 1205, 1155 and 1048 cm⁻¹. The NMR in $CDCl_3$ showed signals at δ 1·30 (3H, *t*, *J*=7 Hz, $COOCH_2CH_3$), 4.2 (2H, *q*, $COOCH_2CH_3$), 2.90 (3H, *d*, *J*=4.5 Hz, CH_3NHCO) and 7.70 ppm (2H, *b*, 2N*H*CO). Its mass spectrum lacked the moleular ion and showed the most intense peak at *m/e* 145 (M-1 ion) and other principal peaks at *m/e* 62, 58 and 45 (scheme).



Scheme

The structure was finally confirmed through its synthesis by condensation of ethylchloroformate with methylurea[3] as also by the action of diazomethane on ethylallophanate.

It is thus envisaged that I is formed by the action of methylisocyanate, a contaminant in the preparation of diazomethane recently shown[4] to lead to undersirable side products, on ethylcarbamate (II) or less likely by N-methylation[5] of ethylallophanate (III) by diazomethane itself (Scheme). Alcoholic decomposition of nitrosomethylurea has been reported[6] to give III apparently by the self condensation of II initially formed by the interaction of alcohol with cyanic acid[7].

Preparation of Ethyl-N-methylallophanate (I)

(i) *From methyl urea* :

Methylurea (3 g) prepared according to Davis and Blanchard[8] was condensed with ethylchlorofor-

mate (4.5 ml) under reflux for 3 hr on water-bath and worked up following the procedure of Biltz and Jeltsch[3]. Crystallization from light petrol afforded ethyl-*N*-methylallophanate (0.5 g), m.p. 134°, $[\alpha]_D \pm 0°$ exactly identical (m.p., m.m.p., IR) with the compound A[1]. (Found: C, 41.14; H, 6.92; N, 19.15. $C_5H_{10}N_2O_3$ requires C, 41.09; H, 6.89; N, 19.17%). *m/e* (rel intensity%) 145(100), 131(1), 117(5), 100(6), 90(3), 89(3), 88(4), 74(4), 70(4), 62(50), 58(78) and 45(32).

(ii) *From ethylallophanate*:

Ethylallophanate (0.2 g) prepared[8] from urea and ethyl chloroformate was dissolved in abs. EtOH (175 ml) and CH_2N_2 liberated from nitrosomethylurea[2] (1 g) in ether was added to it. The reaction mixture was left for 2 hr at room temperature, solvent distilled and boiled with light petrol. The residue (0.17 g) was unconverted ethylallophanate while the desired product, m.p. 134° was obtained (12%) from the solvent phase on chromatography through neutral alumina.

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3-(2-Naphthyl)-1-phenyltriazene 1-oxide as Gravimetric Reagent for Palladium(II)

P. D. Chatlangya, C. S. Bhandari and N. C. Sogani*

Chemistry Department, University of Rajasthan, Jaipur (India)

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Sogani et al[1,2,3] have recommended 3-hydroxy-1, 3-diphenyltriazene (compound I) for the gravimetric determination of palladium. We have now examined 3-(2-naphthyl)-1-phenyltriazene 1-oxide (compound II) and 3-(2-naphthyl)-1-methyltriazene 1-oxide (compound III) as gravimetric reagents for the same purpose. Metal chelates formed by these reagents are granular, insoluble in water, intensely coloured, thermally stable, of definite composition and suitable for direct weighing. Palladium complexes obtained from these reagents are more stable than that from reagent I. In addition, reagent II has more favourable conversion factor and thus offers a distinct advantage over reagents I and III. Hence, it is considered as a superior reagent for palladium estimation.

Preparation of the reagent:

The reagent is prepared by coupling in molar proportion 2-naphthalene diazonium chloride with phenylhydroxylamine in acetate buffered medium at 0°. The crude product is crystallised from benzene, m.p. 180°.

Reagent solution:

One gram of the reagent is dissolved in 100 ml of 0.5% alcoholic KOH.

Procedure for determination:

An aliquot of the solution, containing 10 to 25 mg of the metal, is diluted to 100 ml with distilled water. 5.0 ml of 10% w/v sodium acetate is added to it. Requisite amount of 1*N* HCl is then added to bring the *p*H between 2.5 and 3.5. To this solution, which may also contain varying quantities of foreign ions, reagent solution (20 to 25% in excess to that required by stoichiometry; metal to ligand, 1:2) is added. Palladium complex separates out as a green precipitate. The suspension is heated on a boiling water bath with occasional stirring for 30-35 min. The complex becomes granular and its colour changes to greenish-yellow. It is filtered using a G3 sintered crucible, washed with 25% hot aqueous-alcohol, until the washing gives no colour with 1% NaOH solution. Triazenes develop an intense yellow colour with dil. NaOH solution. The precipitate is finally washed with 95% alcohol and dried to a constant weight at 120-125° for an hour. Conversion factor, 0.1687.

Adopting the above procedure, 10 to 25 mg of palladium has been gravimetrically determined in presence of 0.1 g of cobalt (II), nickel (II), zinc (II), manganese (II), cadmium (II), mercury (II), beryllium (II), magnesium (II), lead (II), aluminium (III), arsenic (III), chromium (III), thorium (IV), rhodium (IV), ruthenium (III), uranyl (II), tungstate, phosphate, fluoride, alkali and alkaline earth metals. The interference of zirconium (IV), tin (IV), titanium (IV) and molybdate is masked with sodium fluoride, and that of bismuth (III) and antimony (III) with sodium potassium tartrate. Hydrolysis of cerium (IV) is prevented by adding a small amount of solid ammonium sulphate. To separate palladium from platinum upto ten times its own weight, the method of Sogani et al.[1] has been successfully employed. Gold (III), silver (I), tin (II), vanadium (IV) and vanadate interfere in palladium estimations Cyanide, more or less, completely masks the precipitation.

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Dielectric Polarizations of Mixtures of Chlorobenzene with Cyclohexane, o-Xylene, m-Xylene, and p-Xylene

M. S. DHILLON

Department of Chemistry, Guru Nanak Dev University, Amritsar, Punjab (India)

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DIELECTRIC polarizations of chlorobenzene with cyclohexane, *o*-xylene, *m*-xylene, and *p*-xylene have been measured at 303.15 K as a function of composition. Dielectric polarizations results show that charge transfer type complexes are formed in these mixtures except in the mixture of chlorobenzene + cyclohexane.

Excess volume V^E of the above mentioned mixtures were reported earlier[1,2]. In this paper, we report dielectric polarizations of the same mixtures at 303.15 K. Dielectric polarizations may provide information about complex formation in solution. The nature of the complex and stability constant of the complex in solution phase can also be ascertained from dielectric polarizations.

Experimental

Cyclohexane, *o*-, *m*-, and *p*-xylenes (all B. D H. grade) and chlorobenzene (Reidel) were purified as described earlier[3,4]. The purities of the samples were checked by measuring their densities; the results agreed to within 0.00002 g cm^{-3} with those in literature[5,6].

Dielectric constants of the pure components and their mixtures were determined from capacity measurements using Universal Impedance bridge (type 01-02a, Toshniwal make) at 303.15 K as a function of composition. The samples were placed in a cell containing a coaxiall brass cylinder. The mouth of the cell can be closed with a glass stopper to eliminate errors due to evaporation. The cell was immersed in a water-filled thermostat controlled to within 0.01 K with the help of toluene regulator and an electronic relay. The measured dielectric constants were correct to within 0.001.

Results and Discussion

The dielectric constants of the pure components and mixtures are recorded in Table 1 at 303.15 K.

The molar polarizations of the mixtures were calculated using the relation[7]

$$P_{12} = (\epsilon_{mix} - 1)/(\epsilon_{mix} + 2).\ \frac{xM_1 + (1-x)M_2}{d} \quad ...(1)$$

where P_{12} is the molar polarization of the mixture, ϵ_{mix} is the dielectric constant of the mixture, d the density of the mixture, x and $(1-x)$ are the mole fractions of the components 1 and 2 with moleculars weights M_1 and M_2.

The molar polarization of the mixture P_{12}, calculated from equation (1) were used in calculating the apparent polarization (P_1 or P_2) of the component from the equation

$$P_{12} = x.P_1 + (1-x).P_2 \quad ... \quad ... \quad (2)$$

by assuming the molar polarization of the other component equal to the value for the pure liquid. The values of apparent polarizations so determined are recorded in Table 1.

TABLE—1 DIELECTRIC CONSTANTS AND MOLAR POLARIZATIONS OF MIXTURES CONTAINING CHLOROBENZENE AT 303.15 K

x	ε	P_{12}/cc	P_1/cc	P^E/cc	$\left(\frac{\epsilon-1}{\epsilon+2}\right)^2$
Chlorobenzene + (1 − x) *o*-xylene					
1	5.560	68.638	–	–	–
0.9063	5.386	67.866	70.427	1.621	0.3626
0.8118	5.182	65.855	71.124	2.818	0.3391
0.7125	4.802	64.508	73.136	3.604	0.3124
0.6209	4.505	63.203	75.461	4.236	0.2903
0.5184	4.276	60.926	77.461	4.574	0.2725
0.4177	3.912	58.368	79.614	4.585	0.2477
0.3144	3.684	54.983	80.840	3.835	0.2230
0.2165	3.400	51.489	81.751	2.839	0.1976
0.0968	2.906	47.298	86.221	1.702	0.1509
0	2.540	43.127	–	–	–
x chlorobenzene + (1—x) *m*-xylene					
1	5.560	68.638	—	—	—
0.9077	5 379	67.892	70.884	2.038	0.3522
0.8137	5.106	66.483	72.859	3.438	0.3328
0.7199	4.823	64.854	74.604	4.666	0.3139
0.6306	4.587	63.425	78.043	5.931	0.2965
0.5305	4 272	60.607	80.198	6.133	0.2721
0.4233	3.902	57.408	83.209	6.168	0.2418
0.3212	3.555	53.226	84.410	5.066	0.2155
0.2154	3.200	49.049	87.583	4.081	0.1790
0.1132	2.836	44.527	91.977	2.642	0.1447
0	2.355	38.470			
x chlorobenzene + (1 − x) *p*-xylene					
1	5.560	68.638	—	—	—
0.9076	5.400	68.337	71.233	2.354	0.3535
0.8105	5.183	67.065	74.176	3.488	0.3391
0.7152	4.802	64.608	75.740	5.079	0.3124
0.6167	4.398	61.850	77.507	5.469	0.2921
0.5198	4.000	58.841	79.339	5.562	0.2500
0.4934	3.889	57.856	79.626	5.422	0.2406
0.4228	3.586	54.940	79.905	4.764	0.2143
0.2942	3.186	50.503	83.729	4.440	0.1777
0.1875	2.804	45.503	86.853	2.853	0.1410
0.1036	2.412	42.483	92.927	2.516	0.1024
0	2.254	36.653			
x chlorobenzene + (1 − x) cyclohexane					
1	5.560	68.638	—		
0.8966	5.106	65.605	70.003		
0.7936	4.716	62.686	71.850		
0.6898	4.235	58.568	72.624		
0.6551	4.142	57.686	73.485		
0.4951	3.603	51.897	76.827		
0.3991	3.326	47.724	78.248		
0.2937	3.000	42.669	79.264		
0.1933	2.681	37.915	81.585		
0.0924	2.402	32.770	83.409		
0	2.007	27.451	—		

Molar polarizations of chlorobenzene in *o*-xylene, *m*-xylene, and *p*-xylene increases at infinite dilutions, indicating the complexing nature of chlorobenzene

in these mixtures. Molar polarization of chlorobenzene in cyclohexane is linear even at great dilutions indicating the absence of complex formation between chlorobenzene and cyclohexane.

The complexes in mixtures, of ohlorobenzene + *o*-, +*m*-, and +*p*-xylenes, may not be formed due to dipole association because exces polarizations, P^E, are positive in these mixtures.

P_{12} is a linear fuction of $(\varepsilon-1)^2/(\varepsilon+2)^2$ which shows that no chemical interaction occurs between the components of the solution. It is expected that only contact-pairs are present.

P^E is again a linear function of $x(1-x)$ for chlorobenzene + *o*-, +*m*-, and + *p*-xylenes which indicate the presence of contact-pairs[9] in these mixtures. It is expected that contact-pairs may be formed between the vacant 3d orbitals of chloro group in chlorobenzene and π-electron cloud of benzene ring in xylenes.

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Temperature Dependent Paper Chromatography of Co(II), Ni(II), Fe(III), Zn(II) and Mn(II)

B. K. DESHMUKH, S. B. GHOLSE, (Miss) V. S. JAWARE and R. B. KHARAT*

Department of Chemistry, Nagpur University, Nagpur-440 010

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TEMPERATURE dependent paper chromatographic separation has been carried out by many workers[1-6]. The results indicate that the speed of resolution is improved by increasing temperature. The purpose of this communication is to employ the known solvent systems *viz*, (i) acetone : HCl : water (87 : 8 : 5)[7], (ii) acetone : HCl (97 : 3)[8] and (iii) acetone : HCl : IBMK (85 : 5 : 10)[9] to study the separation of different cations (a) Co(II), Ni(II) and Fe(III), (b) Co(II), Ni(II) and Zn(II) and (c) Co(II), Ni(II) and Mn(II) at different temperature.

Experimental

All the chemicals used were of AnalaR quality. The usual spraying reagents[10] were used to locate the cations. The solvent mixtures used were (i) acetone : HCl : Water (87 : 8 : 5), (ii) acetone : HCl (97 : 3) and (iii) acetone : HCl : IBMK (85 : 5 : 10). Thermostatic bath with an automatic temperature control was employed to attain a desired temperature. Whatman No. 1 paper was used in glass jar for running the chromatogram.

5.0 μl of the mixture of the cations *viz*., (a) Co(II), Ni(II) and Fe(III), (b) Co(II), Ni(II) and Zn(II), and (c) Co(II), Ni(II) and Mn(II) was enacted in the chromatographic separation.

Results and Discussion

The R_f dependence of various cations on temperature in solvent mixture acetone : HCl : water (87 : 8 : 5) resulted the Table-1, the perusal of which shows that in all cases R_f of Ni (II) remains almost constant from 0^0 to 35^0 and increases slightly from 35^0 to $40°$. R_f of Fe(III), Zn(II) and Mn(II) show same behaviour with slight increase in R_f from 0^0 to 10^0 and running with solvent front above 10^0. This tendency of these three ions to move along with the solvent front depends upon the quality of paper, the nature of the solvent and the temperature at which the experiment is conducted. R_f of Co(II) increases from 0.2 at 0^0 to about 0.8 at 40^0 which means that Co (II) has a tendency to reach solvent front as the temperature rises. Thus, separation in all the three cases is improved by increase in temperature. However, after 35^0, Co(II) reaches Fe(III), or Zn(II) or Mn (II) as the case may be, thereby after $40°$ the separation of these ions may become impossible as suggested by earlier workers[11].

TABLE—1 TEMPERATURE DEPENDENCE OF Rf OF CATIONS, FOR SOLVENT MIXTURE ACETONE: HCl : WATER (87:8:5), TIME = 90 MIN.

System	Ions	Rf valuet at different temperatures(°C)						
		0	10	15	20	30	35	40
	Ni(II)	0.08	0.08	0.08	0.08	0.08	0.08	0.15
1	Co(II)	0.26	0.35	0.40	0.45	0.46	0.69	0.77
	Fe(III)	0.89	0.95	0.95	0.95	0.95	0.95	0.96
	Ni(II)	0.09	0.09	0.09	0.09	0.09	0.09	0.19
2	Co(II)	0.27	0.38	0.41	0.50	0.52	0.70	0.87
	Zn(II)	0.89	0.94	0.94	0.94	0.94	0.94	0.95
	Ni(II)	0.08	0.08	0.08	0.08	0.08	0.15	0 21
3	Co(II)	0.35	0.37	0.46	0.58	0.61	0.83	0.87
	Mn(II)	0 82	0.95	0.95	0.95	0.95	0.95	0.25

A change in temperature influences the rate of movement of the mobile phase as investigated by Muller and Clogg[12]. The rate of movement of given cation and hence its R_f value depends upon its

partition coefficient between the stationary phase and mobile phase. This basic idea of Martin et al[13,14] and Wark[15] resulted the equation :

$$\left(\frac{d \ln \kappa}{dT}\right)_P = \Delta H/RT^2 \ldots\ldots\ldots\ldots\ldots(1)$$

were κ = the partition coefficient.
$\Delta H = H_s - H_m$ = Heat of partition required to transport one gm. mole of the solute from stationary phase to mobile phase. A solution of this expression combined with the equation of Martin and Synge[13] gives a relationship given by Bate-Smith and Westall[16].

$$R_m = \log\left(\frac{1}{R_f} - 1\right) = \frac{-\Delta H}{2.303RT} + K \ldots\ldots(2)$$

where K is an arbitary constant.

The plots of R_m vs. 1/T are linear over a temperature range $-5°$ to 40° indicating its applicability. The plots exhibit positive stope assigning negative values to the heat of partition (Table-2). Table-2 suggests that the ΔH for Fe(III), Zn(II), and Mn(II) are zero. This might be due to not holding equation (2) in these cases. However, for Fe(III), Zn(II) and Mn(II), increase in R_f from 0° to 10° can be predicted with the small increase in ΔH, which remains constant above 10° as evinced by their movement along with the solvent front (Table-1).

TABLE—2 HEAT OF PARTITION OF CATIONS, FOR SOLVENT MIXTURE ACETONE : HCl : WATER (87 : 8 : 5), TIME—90 MIN.

System	ΔH value in KCal/mole				
	Fe(III)	Co(II)	Ni(II)	Zn(II)	Mn(II)
Fe(III) + Co(II) + Ni(II)	0.0	-9.64	0.0	-	-
Zn(II) + Co(II) + Ni(II)	-	-9.57	0.0	0.0	-
Mn(II) + Co(II) + Ni(II)	-	-9.61	0.0	-	0.0

Practically zero value of ΔH for Ni(II) in all three systems would mean that at equilibrium the partition coefficient approaches a unit value and the concentration of species equals in both the phases. The tendency to pass over from one phase to another should remain unaffected by variation in temperature. Thus, practically zero value of ΔH for Ni(II) and high instability of its chloro complex leads Ni(II) to remain at its original position. There is apparent increase in R_f value of Ni(II) from 35° to 45° which might not be due to migration of Ni(II), but as temperature increases, solvent gets evaporated and thus solvent front does not rise much. This causes apparent increase in R_f .

A relatively higher value of ΔH for Co(II)in all three systems indicates its tendency to pass into mobile phase from stationary phase with an increase in temperature. Increase in R_f of Co(II) with increase in temperature supports this idea (Table-1).

Investigation of the system (a) Co(II), Ni(II, and Mn(II) in solvent system acetone : HCl (97 :3) reveals that R_f of Ni(II) remains constant over the studied temperature range. R_f of Mn(II) changes from 0.75 at -5° to 0.98 at 20° and thereafter attaining unit value at higher temperature. Thus, this system shows clear separation from -5° to 15° afterwhich Co(II) touches Mn(II). This tendency of Co(II) and Mn(II) of passing together above 15° indicates their equal ΔH values.

It was observed that R_f values of Ni(II) remain practically constant (0.03) within the temperature range of 0° to 30° in all three cations systems, in the solvent system acetone : HCl : IBMK (85 : 5 : 10) as although there is slight apparent increase in R_f beyond 30° (0.05) as discussed earlier. All the three cations viz. Fe(III), Zn(II), Mn(II) have similar tendency to pass along with the solvent front at all temperature. The R_f values of Co(II) in all the three systems increase with the temperature (0.40 to 0.80) at 0° to 30° respectively and it was observed that Co(II) has a tendency to attain unit value of R_f beyond temperature 30°.

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Titrimetric Determination of Hydrogen Peroxide and Sodium Perborate by Periodate

R. L. KAUSHIK,* O. P. VERMANI and RAJENDRA PROSAD

Chemistry Department, Regional Engineering College, Kurukshetra (Haryana)

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HUCKABA and Keyes[1] determined hydrogen peroxide with permanganate in acid medium. Willard and Young[2] obtained good results with ceric sulphate. Perborate reacts with potassium permanganate and ceric sulphate in the same way as hydrogen peroxide. Schwicker[3] reduced periodate to iodate in alkaline medium with hydrogen peroxide. It has been observed in the present investigation that if periodate is taken in excess, hydrogen peroxide and sodium perborate are quantitatively oxidised.

$$IO_4^- + H_2O_2 \rightarrow IO_3^- + H_2O + O_2 \quad \ldots \quad (1)$$
$$IO_4^- + BO_3^- \rightarrow IO_3^- + BO_2^- + O_2 \quad \ldots \quad (2)$$

Periodate can be selectively masked with molybdate whereas iodate remains unaffected[4]. The same masking effect has been utilised in the determination of iodate formed by periodate oxidation of hydrogen peroxide and sodium perborate (eq. 1 and 2). The reaction products in each case are treated with potassium iodide in presence of chloroacetic acid buffer after masking periodate with molybdate :

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O \quad \ldots \quad (3)$$

Since the iodate formed is stoichiometrically related to the amount of the substance taken, the liberated iodine can be represented by

$$H_2O_2 \approx NaBO_3 \approx 3I_2$$

The titration of the liberated iodine makes the method highly sensitive and suitable for the determination of small amounts of the substances.

Experimental

All the chemicals used were of analytical grade commercially available. Solutions of hydrogen peroxide and sodium perborate were prepared by dissolving these substances in distilled water and standardised iodometrically.

Buffer solution was prepared by dissolving 25 g of chloroacetic acid in 70 ml distilled water and its pH adjusted to 2.9 with a strong solution of sodium hydroxide.

2 M molybdate solution was prepared by dissolving ammonium molybdate in hot distilled water.

Procedure :

A suitable aliquot of the substance to be determined was pipetted into an Erlenmeyer flask containing an excess of potassium metaperiodate (50-100 mg). The contents of the flask were shaken for 2-3 min and 10 ml of 2 M ammonium molybdate followed by 10 ml of chloroacetic acid buffer were added. 1 g of potassium iodide was then added and contents of the flask thoroughly mixed. The liberated iodine was titrated with 0.1 N sodium thiosulphate solution. The results are given in the Table. 1

TABLE 1 DETERMINATION OF HYDROGEN PEROXIDE AND SODIUM PERBORATE

Taken	*Found*	*Error*
	Hydrogen Peroxide (mg)	
4.72	4.70	−0.02
5.50	5.50	0.00
6.57	6.55	−0.02
7.08	7.08	0.00
7.99	8.02	+0.03
8.96	9.01	+0.05
	Sodium Perborate (mg)	
20.66	20.66	0.00
24.10	24.23	+0.13
27.54	27.54	0.00
31.52	31.37	−0.15
35.46	35.45	−0.01
39.40	39.53	+0.13

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Study of Cucumis melo utilissimus Seed Oil

S. P. TANDON, Chemistry department, University of Allahabad, Allahabad
and
S. Q. HASAN*, Chemistry department, Pt. J. N. College, Banda

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CUCUMIS MELO UTILISSIMUS Duthie and Fuller known as *Kakri* in hindi belongs to the family cucurbitaceae. Seeds are cooling, nutritious, diuretic and used in painful micturition and suppression of urine[1]. It is cultivated in many parts of India, specially in upper India and particularly in Uttar Pradesh and Punjab[2]. The present work deals with the chemical investigation of the seed oil of *Kakri* which has not been reported so far. Taking into account the medicinal use of the seed of the plant information on general characteristics and fatty acid

*For correspandence

composition is of utmost importance. The main objective of the work was to correlate the fatty acid composition and unsaponifiable matter in the seed oil to its medicinal uses.

Experimental :

Authentic samples of *Jaunpury Kakri* seeds were used in the present investigation. 600 g air dried seeds were broken by suitable methods. The oil content was determined in a continuous soxhelet extractor using petroleum ether (60-80) as solvent. This was purified by filtering through animal charcoal and drying over anhydrous sodium sulphate. The characteristics of the oil were determind by conventional methods. The results are presented in Table 1. 100 g oil were mixed with excess of alcoholic KOH and boiled for eight hours over a water bath. The alcohol was distilled off and the soap was dissolved in excess of water. The

TABLE—1 CHARACTERISTICS OF OIL SEEDS AND OIL

Moisture %	7.5
Oil %	32.00
Oil % (on kernel)	41.00
Colour of oil	Yellow
Refractive Index at 30°	1.4200
Specific gravity at 31°	0.902
Acid value	8.8
Saponification value	226.4
Saponification equivalent	247.8
Iodine value	94.2
Consistency	Liquid
U. M.	0.81%

unsaponifiable matter was separated by filtration. Then the soap solution was extracted with ether. This removed any remaining unsaponifiable matter. The soap solution was treated with dil. sulphuric acid and the mixture was heated for a few minutes. The liberated fatty acids were taken in a separating funnel after dissolving the fatty acids in ethyl ether. The ethereal solution of fatty acids was washed several times with water to free it from impurities. Ether was distilled off and a mixture of fatty acids obtained. The mixed fatty acids were separated into solid and liquid acids by Twithells Lead salt method modified by Hilditch.

The saponification and iodine values of the mixed fatty acids (Solid and Liquid) were determined separately and presented in a tabular form (Table 2).

TABLE—2 CHARACTERISTICS OF SOLID AND LIQUID FATTY ACIDS

	Solid fatty acids	Liquid fatty acids
%	22%	78%
Iodine value	22.5	98.0
Saponification value	242.2	212.6
Saponification equivalent	231.6	268.6

The quantitative and qualitative composition of the component acids of the mixed fatty acids are determined by methyl ester distillation, urea adduct fractionation and paper chromatographic methods.

TABLE—3 FRACTIONAL DISTILLATION OF SOLID FATTY ACID METHYL ESTERS

Total weight of esters = 12.2 g

Fractions	Distillation temp. in°C	Weight of acids in g	S.V. of acids	S.E. of acids	I.V. of acids
1	150-165	1.5	303.1	185.1	30.0
2	165-180	2.055	248.4	225.8	26.2
3	180-195	3.95	208.8	268.7	20.5
4	195 and above	3.06	203.5	275.6	30.2

Pressure = 10 mm.

TABLE—4 FRACTIONAL DISTILLATION OF LIQUID FATTY ACID METHYL ESTERS

Total weight of esters = 44.5 g

Fractions	Distillation temp. in°C	Weight of acids in g	S.V. of acids	S.E. of acids	I.V. of acids
1	150-160	4.725	202.0	277.7	80.1
2	160-170	8.62	201.1	278.9	114.8
3	170-180	15.40	201.2	278.8	123.1
4	180-and above	10.69	201.3	278.7	142 8

Pressure = 10 mm.

TABLE—5 FATTY ACID COMPOSITION OF THE OIL

Species	8:0	10:0	12:0	14:0	16:0	16:1	18:0	18:1	18:2
Cucumis melo utilissimus	1.2	0.8	2.0	0.91	13.1	0.73	3.96	44.1	33.2

Results and discussion

Cucumis melo utilissimus seed oil (32.00% on seed, 41.00% on kernel) is yellow in colour. The major fatty acid components of the oil are Oleic acid (44.1%) and Linoleic acid 33.2%. Palmitic and Stearic acids are present to the extent of 13.1% and 3.36% respectively. The other acids present are Caprylic 1.2%, Capric 0.8%, Lauric 2.00% and Myristic 0.91%. Hexadecenoic acid is present to the extent of 0.73%. High percentage of unsaturated acids is responsible for the cooling effect of seeds. It is the general characteristic of cucurbitaceae family.

Acknowledgement

One of the authers (S.Q. Hasan) is grateful to the State Council of Science and Technology for providing financial assistance for carrying out this work.

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Stepwise Stability Constants of Copper 2-Hydroxy Methyl Benzimidazole in 50% Ethanol

K. S. PATEL, I. M. BHATT* and D. P. DANI
Chemistry Department, University School of Sciences, Gujarat University, Ahmedabad-380009, India

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THE determination of stability constants by e.m.f. measurements of metal in equilibrium with complexes of metal was first attempted by Riley and Gallafent[1]. In the present investigation, Leden method was employed to determine the stepwise stability constants of Cu-2-HMBMA complex in 50% ethanol.

Experimental and Results

The following two cells were set up

Cell-A

− SCE	KNO_3 salt bridge	2 ml 0.01 M $CuSO_4$ +2 ml 1.0 M KNO_3 +4 ml EtOH +12 ml 50% EtOH	+ Cu

Cell-B

− SCE	KNO_3 salt bridge	2 ml 0.01 M $CuSO_4$ +2 ml 1.0 M KNO_3 +4 ml EtOH +x ml 0.1 M HMBMA in 50% EtOH +y ml 50% EtOH (x+y=12 ml)	+ Cu

The potentiometric measurements were carried out at 35±1° using Leeds and Northup potentiometer having accuracy of ±0.1 mV. Copper electrode was prepared[2] and its reversibility was checked from time to time during the measurements. The results are given in Table-1.

TABLE—1

Sr. No.	'X'	'Y'	E_2 Volts	ΔE (E_1-E_2)	(L) $\times 10^3$
1	0.0	12.0	+0.0485(E_1)	–	–
2	1.0	11.0	−0.1157	0.1642	1
3	2.0	10.0	−0.1735	0.2220	6
4	3.0	9.0	−0.1809	0.2294	11
5	4.0	8.0	−0.2132	0.2617	16
6	5.0	7.0	−0.2281	0.2766	21
7	6.0	6.0	−0.2403	0.2888	26
8	7.0	5.0	−0.2485	0.2970	31
9	8.0	4.0	−0.2534	0.3019	36
10	9.0	3.0	−0.2724	0.3209	41

The e.m.f. of Cell-B is given by

$$E_2 = E' + \frac{RT}{nF} \ln (M)$$

where (M) is the free metal ion concentration. In the above equation E' includes the potential of the calomel electrode, the liquid junction potential and the correction term for activity coefficient in the mixed solvent. In the case of Cell-A, when no ligand is added the e.m.f. of the cell is given by

$$E_1 = E' + \frac{RT}{nF} \ln (C_M)$$

where (C_M) is the metal ion concentration. When ligand is added some of the metal ions are removed to form a complex and new potential, E_2 will be set up. Hence,

$$\Delta E = E_1 - E_2 = \frac{RT}{nF} \ln \left(\frac{C_M}{M}\right)$$

$$= \frac{0.06105}{n} \log \left(\frac{C_M}{M}\right) \text{ at } 35°$$

The quantity (C_M/M) is known as the degree of formation and is designated as ϕ, so that,

$$\log \phi = \frac{nF}{2.303RT} \cdot \Delta E$$

According to Leden[3],

$$F_n(L) = \frac{F_{n-1}(L) - \beta_{n-1}}{(L)} = \beta_n$$

From the above equation it is easy to calculate $F_n(L)$

TABLE—2

Sr. No.	$\left(\frac{C_M}{M}\right)$	$F_1(L)$	$F_2(L)$	$F_3(L)$ $\times 10^{-14}$	$F_4(L)$ $\times 10^{-16}$
1	–	–	–	–	–
2	2.410×10^5	2.411×10^8	7.500×10^{10}	0.147	2.730
3	1.905×10^7	3.174×10^9	5.012×10^{11}	0.735	10.240
4	2.856×10^7	2.597×10^9	2.234×10^{11}	0.148	0.256
5	3.784×10^8	2.365×10^{10}	1.468×10^{12}	0.880	4.750
6	1.169×10^9	5.541×10^{10}	2.630×10^{12}	1.224	5.251
7	2.951×10^9	1.134×10^{11}	4.361×10^{12}	1.654	5.899
8	5.470×10^9	1.764×10^{11}	5.790×10^{12}	1.848	5.573
9	7.943×10^9	2.206×10^{11}	6.127×10^{12}	1.684	4.344
10	3.311×10^{10}	8.075×10^{11}	1.970×10^{13}	4.790	11.390

* Serial numbers correspond to those given in Table 1

Discussion

If F_1 (L) is plotted versus (L), the intercept will be β_1 and slope will be β_2. Similarly if F_2 (L) is plotted versus (L), limiting slope will be β_3 and intercept will be β_2. Hawkins and Perrin[4] have reported stability constants of copper benzimidazole. The values of log K_1, log β_2, log β_3 and log β_4 at ionic strength of 0.15 *M* $NaClO_4$ were 3.56, 6.34, 9.0, 10.91. The values of log K_1 and log K_2 were 3.56 and 2.78. In the present case, log K_1 and log K_2 of copper-2-HMBMA are 8.22 and 2.56. The lower value of log K_2 for Cu-2-HMBMA complex may be due to the steric effect of 2-substituent. From the

*Correspondence to be addressed to.

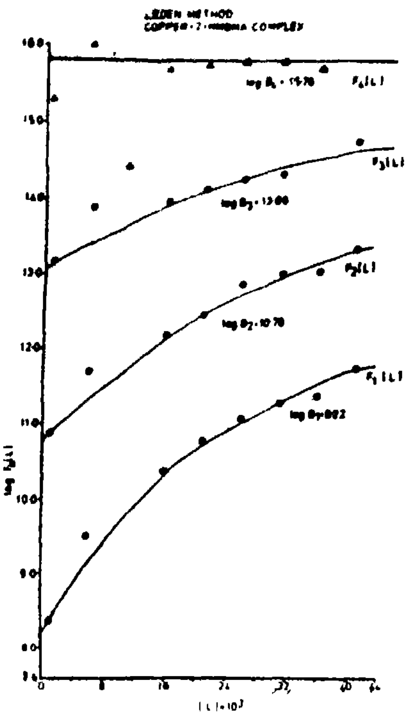


figure the stepwise stability constants will be as given below ;

Complex	Log K_1	log K_2	log K_3	log K_4
$Cu(HMBMA)_4SO_4$	8.22	2.56	2.30	2.70
			log β_4=15.78	

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Nickel (II) Complexes of some new Tridentate (ONN) Dibasic Schiff Bases

NITYANANDA SAHA and B. N. MALLICK

Department of Pure Chemistry, University College of Science, Calcutta-700009

Manuscript received 4 March 1977, accepted 21 March 1977

ALTHOUGH transition metal complexes of salicyldehyde schiff bases have been extensively studied [1,2], very little work has been reported[3] particularly on the coordination behaviour of ONN donor tridentate schiff bases (derived from salicyldehyde). This preliminary communication reports syntheses and characterisation of several nickel(II) complexes with four new schiff bases derived from salicyldehyde or 5-substituted salicyldehyde and nitroaminoguanidine.

Experimental

(A) *Syntheses of schiff bases :*

All the four schiff bases were prepared by refluxing a mixture of aqueous alcoholic solutions of nitroaminoguanidine (0.01 mole) and R-salicyldehyde (0.01 mole) (R=H, 5-Cl, 5-Br and 5-NO_2) for one hour. The schiff bases (R-SBH_2) having light yellow colour with varying shades, are insoluble in water but soluble in aqueous alcohol (R=5-Cl, 5-Br) or in alkaline alcoholic solution (R=H, -5NO_2) Anal : R-SBH_2 :

(a) R=H m.p. 220° (d), (Found : N, 31.80 ; C, 42.84 ; H, 3.82. Calcd for $C_8H_9O_3N_5$: N, 31.45 ; C, 43.05 ; H, 4.03%)

(b) R=5-Cl m.p. 225° (d), (Found : N, 27.52 ; C, 37.42 ; H, 2.90. Calcd for $C_8H_8O_3N_5Cl$, N, 27.18 ; C, 37.28 ; H, 3.10%)

(c) R=5-Br m.p. 227° (d), (Found : N, 22.98 ; C, 31.52 ; H, 2.44. Calcd for $C_8H_8O_3N_5Br$, N, 23.18 ; C, 31.79 ; H, 2.65%)

(d) R=5-NO_2 m.p. 252° (d), (Found : N, 31.68 ; C, 35.60 ; H, 2.72. Calcd for $C_8H_8O_5N_6$, N, 31.34 ; C, 35.83 ; H, 2·98%)

(B) *General method for the syntheses of the complexes :*

(i) [NiR-SB H_2O]n H_2O (R=H, 5-Cl, 5-Br, 5-NO_2)

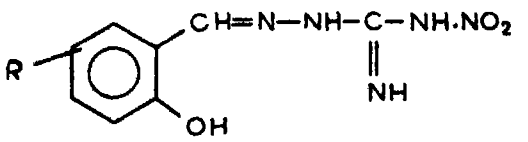
On mixing either an alcoholic solution (R=5-Cl, 5-Br) or an alkaline alcoholic solution (R=H, 5-NO_2) of the schiff base (0.01 mole) with an aqueous alcoholic solution of $NiCl_2$, $6H_2O$ (0.01 mole), a deep red solution resulted, when the *p*H of the solution was adjusted to 6~7 by addition of dil NaOH or ammonia solution whenever necessary. The resulting solution was refluxed for one hour and the orange-red compound, in each case, was collected on the filter, washed with ethanol and dried in a desiccator over silica gel.

(ii) [NiR-SBX]nH_2O (X=py, β-picoline and γ-picoline)

These mixed ligand complexes were prepared either by reaction of the corresponding aquo-variety (suspended in alcohol) with the respective base and subsequent evaporation of the resulting solution on water bath or by refluxing a mixture of schiff base (0.01 mole), $NiCl_2$, $6H_2O$ (0.01 mole) and the corresponding base (0 01 mole) in aqueous alcoholic or alkaline ethanolic solution. In each case, an orange-yellow compound was collected, dried as before by washing with alcohol and acetone.

Results and Discussion

The schiff bases, R-SBH$_2$, having given the structural formulation I from elemental analyses, are also recognised from i.r. spectra which exhibit most characteristic bands in the 3μ region (3400 and 3200 cm^{-1}), at 1600 cm^{-1} and also at 1260 cm^{-1} attributable to $-$NH, C=N and C$-$O stretching vibrations respectively[4,5].



R=H, 5-Cl, 5-Br, 5-NO$_2$

I

All the nickel (II) complexes [NiR-SBX]nH$_2$O, (X=H$_2$O, py, β and γ-pic) show in their i.r. spectra, a single broad band at 3380 cm^{-1} indicating involvement of the nitroguanyl group (with deprotonation) in complexation[6]; moreover, lowering of $-$C=N and increase of C$-$O stretching frequencies in the complexes as compared to the free ligand point to the participation of the azomethine and phenolic $-$OH group in bonding with the metal[5,7].

All the present orange-red Ni (II) complexes are diamagnetic as ascertained from magnetic susceptibility measurements (Gouy method using G.R. CuSO$_4$, 5H$_2$O as calibrant). The mull spectra (recorded in liquid paraffin in a Hilger Uvispek spectrophotometer) of the complexes show a principle absorption band between 22,500-24,500 cm^{-1} (Table 1) which may be attributed to $^1B_1 \leftarrow {}^1A_1$ transition[8] in a square-planar geometry. The insolubility of the complexes in water and innocent organic solvents and in some cases in donor solvents suggest strong association between the planar molecules in the solid state. In a few cases the solution of the complexes in a donor solvent like pyridine does not show any spectral change and this lack of solvation or coordination (by a solvent) may be ascribed to the strong ligand field favoring square planar configuration.

Detailed studies of the coordination behaviour of these and other schiff base ligands derived from nitroaminoguanadine transition with metal ions are in progress.

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TABLE—1 ANALYTICAL AND ELECTRONIC SPECTRAL DATA OF [NiR-SBX].nH$_2$O

R	X	n	% of Ni Found	% of Ni Calcd.	% of N Found	% of N Calcd.	Electronic spectra (mull) λ_{max} (cm^{-1})
H	H$_2$O	3	16.45	16.64	19,95	19.90	23,500 ; 15,630 (sh)
,,	Py	2	14.97	14.87	20.75	21.27	23,260 ; 16,400 (sh)
,,	β-pico	2	15.92	14.36	17.96	17.12	23,260 ; 16,130 (sh)
,,	γ-pico	2	14.30	14.36	17.15	17.12	23,530 ; 14,810 (sh) 11,910 (s h)
5-Cl	H$_2$O	1	17.02	16.76	19.43	19.99	23,530 ; 15,380 (sh)
,,	Py	1	13.76	14.28	21.02	20.43	22,730
,,	β-pico	0	14.86	14.41	20.42	20.63	23,260 ; 15,630 (sh)
,,	γ-pico	1	13.73	13.80	20.22	19.75	23,260
5-Br	H$_2$O	1	14.72	14.87	18.20	17.73	24,390 ; 15,630 (sh)
,,	Py	1	12.79	12.88	18.31	18.44	23,500
,,	β-pico	1	12.32	12.49	17.69	17.88	24,000
,,	γ-pico	0	12 79	12.99	18.92	18.60	23,820 ; 15,630 (sh)
5-NO$_2$	H$_2$O	1	16.53	16.28	23.04	23.29	24,390
,,	Py	0	15.06	14.88	23.81	24.28	23,580
,,	β-pico	0	15.20	14.06	23.14	23.46	22,600
,	γ-pico	0	14.17	14.06	23.09	23.46	23,500

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Protonation Constants of Salicylic and Substituted Salicylic Acids

P. V. KHADIKAR, School of Studies in Chemistry, Vikram University, Ujjain (M. P.), India
and
P. S. DESHMUKH, Govt. College, Khargone, (M. P.), India.

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THE protonation constants of a few substituted salicylic acids have been reported earlier[1-3]. No attempt seems to have been made to determine the same in 50% (v/v) aqueous ethanol medium. The pK values of Salicylic (SA), 5-Sulpho-salicylic (SSA), 5-Amino-salicylic (5-NH_2SA), 5-Chlorosalicylic (5-ClSA), 3-Nitro-salicylic (3-NO_2SA), 5-Nitro-salicylic (5-NO_2SA), and 3 : 5 Di-nitro-salicylic (3 : 5-DNSA) acids have, therefore, been determined employing Bjerrum's titration technique as reported by Irving and Rossotti[4]. Refined values are then obtained by point-wise calculation and linear plot methods and are reported here.

Experimental :

All the chemicals used were of B.D.H. AR grade.

Polymetron model CL-41 *p*H-meter was used for *p*H-metric titrations conducted at 30°. Measurments were made with an accuracy of $\pm 0{\cdot}05$ *p*H units and the reproducibility of the readings was of the same order.

*p*H-metric titrations of the solutions of (i) free $HClO_4$ and (ii) free $HClO_4$ + Ligand (acid) were performed in 50% (v/v) aqueous ethanol medium against standard NaOH solution while maintaining the ionic strength at 0·1 *M* ($NaClO_4$).

Results

The Irving-Rossotti[4] expression was used for the calculation of $\bar{n}_A$ values. These in turn were employed for the determination of stepwise dissociation constants of the various salicylic acids used in the present investigation.

The values of *p*K were calculated by half-integral method making use of formation curves. The values of *p*H at $\bar{n}_A = 0.5$ and $\bar{n}_A = 1.5$ correspond to the values of pK_2 and pK_1 respectively. Refined values of pK were also obtained by point-wise calculations and linear plot method and are also recorded in Table – 1.

The *p*K$_1$ value is found to follow the order: SA>SSA>5-NH_2SA>5-ClSA>3-NO_2SA>3 : 5-DNSA in agreement with the inductive effect of the substituents[5]

The results indicate the failure of Hemmett's equation[6-10].

TABLE—1 *p*K VALUES FOR SALICYLIC AND SUBSTITUTED SALICYLIC ACIDS

Ligand (Acid)	Half intergal method			Linear plot method			Point-wise calculation average			Average		
	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3	pK_1	pK_2	pK_3
SA	3.15	11.80	–	3.13	11·64	–	3.33	11.76	–	3.20	11.73	–
SSA	1.94*	3.10	–	1.93*	3.07	11.71	1.98*	3.08	11.70	1.95*	3.08	11.70
5-NH_2SA	2.80	5.45†	11.00	2.80	5.43†	10.99	2.72	5.45*	10.96	2.77	5.44†	10.98
5-ClSA	2.57	11.63	–	2.62	11.46	–	2.68	11.56	–	2.62	11.55	–
3-NO_2SA	2.30	10.35	–	2.35	10.33	–	2.25	10.35	–	2.30	10.34	–
5-NO_2SA	2.25	10.79	–	2.25	10.72	–	2.28	10.75	–	2.26	10.75	–
3:5-DNSA	2.08	8.13	–	2.03	8.18	–	2.01	8.21	–	2.04	8.17	·

*for SO_3H and †for NH_3^+ (the conjugate acid)

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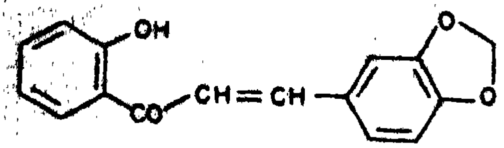
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A new Synthesis of 3-Hydroxy-3′:4′-Methylenedioxy-Flavone

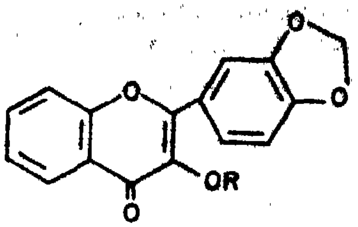
S. P. DHOUBHADEL and S. M. TULADHAR
Department of Chemistry, Tribhuvan University
Kirtipur, Kathmandu, Nepal

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IN our investigations on the flavonoids of the indigenous plants, 3-hydroxy-3′ : 4′-methylenedioxy flavone(II) was needed for comparison. While Hattori[1] prepared it by acid hydrolysis of the oximino derivative of the corresponding flavanone, we herein report an elegant synthesis of the flavonol (II) by the application of Algar Flynn Oyamada (AFO)reaction



(I)



(II, R = H)
(III, R = $COCH_3$)
(IV, R = CH_3)

Claisen condensation of *o*-hydroxyacetophenone with piperonal afforded the chalcone(I) which was subjected to simultaneous cyclisation and oxidation by alkaline hydrogen peroxide to yield II. The structure was proved by melting point, analysis and, spectroscopic data (*vide* Experimental) as well as by preparation of its *o*-methyl and *o*-acetyl derivatives. The NMR spectrum of II deserves special mention. Besides the characteristic signal ar τ 3.97 for $-O-CH_2-O-$grouping, spin decoupling by irradiation at H-5′ and H-5 indicated that H-6′ was ortho coupled to H-5′ and meta coupled to H-2′ H-5 was ortho coupled to H-6 and meta coupled to H-7. H-2′ was hidden in H-6′ signal. H-7 and H-8 signals were overlapped.

Experimental

All m.ps. are uncorrected. UV spectrum was taken on Varian instrument (model 635). IR and NMR spectra were reorded respectively on Unicam SP 1000 and a Varian A-60 Mc NMR (TMS as internal reference) spectrometers Mass spectrum was taken on A.E.I. spectrometer, (Model MS 9).

2′Hydroxy-3 : 4-methylendioxy-chalcone (I) :

o-Hydroxyacetophenone (2.2 ml) and finely powdered piperonal (2.49 g) were mixed. An absolute alcoholic solution (2 ml) of NaOH (2 g) was then added and the mixture was allowed to stand overnight at room temp. The orange red sodium salt obtained was acidified with dil. HCl to get the yellow solid, 2′-hydroxy-3 : 4-methylenedoxy-chalcone recrystallised from alcohol in faint yellowish crystals, m.p. 136-138° (lit.[2] m.p. 138°) ; yield 3.4 g (84.1%). Found : C=71.58 ; H=4.53%, Calc. for $C_{16}H_{12}O_4$, C=71.64 ; H=4.48%.

3-Hydroxy-3′ : 4′-methylenedioxy-flavone (II) :

2′-Hydroxy-3:4-methylenedioxy-chalcone (I : 0.73 g) was dissolved in freshly distilled methanol (68 ml) NaOH solution (20 ml, 4*N*) was added dropwise to the cooled solution with occasional shaking and cooling. Hydrogen peroxide solution (9 ml, 18%) was then slowly added to the mixture with light shaking and left overnight at room temp. The intense yellow flocculent solid flavonol(II) that separated was recrystallised from absolute alcohol in nearly colourless crystals, mp. 212-214° (lit.[1] m.p. 214°) ; yield 0.68 g (88.5%). Found : C=67.90 ; H=3.90% ; Calc. for $C_{16}H_{10}O_5$: C=68.1 ; H=3.55%. $\lambda_{max}^{ethanol}$ 360 nm, (ϵ=42,000) and 245 nm (ϵ=47,000) ; ν_{max}^{nujol} cm^{-1} 3250 (sharp) ; 1570(m) ; 1610 (s) ; NMR ($CDCl_3$) : τ : 3.97 ; s, 2H,—O—CH_2 O—; 1.78, br. d, 1H, *J*=7.8 Hz, H-5 ; 2.16, br, d, 1H *J*=8.0 Hz, H-6′ ; 2.25, hidden s, 1H, H-2′ : 242 ill-defined m, 2H, H-7 and H-8 ; 2.58, br. d, 1H, J=7.8 Hz, H-6 ; 3.06, d, 1H, *J*=8.0 Hz, H-5′. MS : *m/e* 282 (M^+, 100%), 281 (M-H, 36%), 254 (M-CO, 10%), 225 (M-CO and CHO, 10%) and 196 (MCO, and 2CHO, 10%). The compound responder to basic lead acetate and Shinoda colour tests. It produced reddish solution with conc. H_2SO_4 acid and brownish violet colour with $FeCl_3$.

It formed *o*-acetate (III) in colourless needles (ethanol). m.p. 136-137° in the usual way with Ac_2O in pyridine at room temp. left for 2 days. Found : C=66.61 ; H=3.76% ; $C_{18}H_{12}O_6$ requires C=66.63 ; H=3.70%.

3′ : 4′-Methylenedioxy-flavonol-o-methyl ether :

The flavonol (II) 0.11 g), and. K_2CO_3 (2 g), CH_3I (1 ml) in dry acetone (10 ml) were refluxed for 6 hr. Usual work-up yielded a light chrome solid *o*-methylether derivative, recrystallised from ethanol in colourless prisms, m.p. 153° (lit.[1], m.p. 155°) ; yield 0.09 g (77.9%). Found : C=68.84 ; H=4.12%; Calc. for $C_{17}H_{12}O_5$: C=68.92 ; H=4.05%.

Acknowledgements

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Mixed Ligand Complexes of bis(Ethylmalonato) Ni(II) with Nitrogen Donors

B. B. MOHAPATRA, B. K. MOHAPATRA and S. GURU

Department of Chemistry, Ravenshaw College, Cuttack-753003(Orissa)

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BETA-Diketones, esters, beta-keto esters and *o*-hydroxy carbonyl compounds have drawn considerable attention long since as oxygen donor-chelating ligands. We have been attempting[1-8] to prepare mixed ligand complexes with nitrogen and sulfur donors using metal chelates of these ligands. In this communication we report the mixed ligand complexes of heterocyclic amines and Ni(II) malonate.

Experimental

All the chemicals were of AnalaR grade. To an ethanolic solution of Ni(II) chloride, malonic ester was added in stoichiometric ratio and the solution shaken for fifteen minutes. Ammonia was added dropwise and the solution was allowed to stand over night when blue crystalline Ni(II) malonate separated out. It was filtered, washed with ethanol and ether and dried in vaccum.

Mixed lingand complexes were prepared by refluxing and ethanolic suspension of the chelate and amines in 1 : 2 ratio for about 2 hrs over water-bath. On cooling crystalline compounds separated out which were filtered/under suction, washed with ethanol followed by ether and dried in vaccum.

Metal was estimated complexometrically by EDTA titration method and nitrogen by standard microanalytical method. Conductance was measured in M/1000 acetone solution of the complexes by a Toshniwal conductivity bridge. Magnetic susceptibility measurement was made over solid specimen at room temperature (25°) by Gouy method using Hg $[Co(NCS)_4]$ as calibrant. I.R. spectra were recorded on KBr phase using Perkin-Elmer-621 Spectrophotometer. Electronic spectra were recorded in M/100 (chloroform-base) solution using Hilger Watt-U Vispock spectrophotometer. All the relevant analytical and spectral data are recorded in Table-1.

Results and Discussion

Complexes reported in the present investigation have the general formula : $[NiL_2B_2]$ and $[NiL_2B']$ where L is malonic ester and B is a monodentate heterocyclic amine and B' is ethylenediamine. These are blue, green or light violet crystalline compounds, have fairly low melting points and soluble in acetone in which medium they behave as non-electrolytes the Δ_M being in the range of 8-15 mhos cm² μ_{eff} values range between 2.9 to 3.2 B.M. indicating the presence of two unpaired electrons and presumably a spin-free octahedral configuration.

Inportant infrared bands have been assigned. Ni(II) malonate has two absorption bands at 1600 and 1290 cm⁻¹ region attributable to ν(C=O) and ν(C–O) respectively. These two bands occur at a considerable lower frequency in the chelate compared to that of ethyl malonate, indicating bonding through oxygen. In the mixed ligand complexes these two bands are found ~1630 and ~1320 cm⁻¹ region, a shift to the high frequency side indicating bonding of the σ-bonded heterocyclic amines. Moreover, most of the absorption bands due to free nitrogen ligands have been shifted in the complexes. Further bonding of the Ni(II) ion through the oxygen of the ester and nitrogen of the amines is comfirmed by the observation of ν(M—C) and ν(M—N) ~510 and ~330 cm⁻¹ respectively in the far-infrared spectra.

In the electronic spectra of mixed ligand complexes three absorption bands appear around 10-11,

TABLE 1 ANALYSIS, CONDUCTANCE, MAGNETIC SUSCEPTIBILITY, I.R. SPECTRAL (cm⁻¹) AND ELECTONIC SPCTRA K. K. (ε)

Compound	% of Nickel Found	% of Nickel Reqd.	% Nitrogen Found	% Nitrogen Reqd.	Δ mho Cm²	μeff B.M.	ν(C—O)	ν(C—O)	ν(M—O)	ν(M—N)	
$[NiL_2]$	15.24	15.55	—	—	—	—	1600	1290	510		
$[NiL_2Py_2]$	10.72	10.97	5.14	5.23	8.5	2.95	1620	1310	520	330	10(6),15(7). 24(16).
$[NiL_2(\gamma\text{-pic})_2]$	10.26	10.43	4.85	4.97	8.0	3.1	1610	1320	510	330	11.5(7), 15.8(7). 25(17).
$[NiL_2(Pip)_2]$	10.58	10.73	4.96	5.12	11.6	3.05	1620	1315	520	325	11.6(6), 14 8(6), 14.5(15).
$[NiL_2Q_2]$	8.83	9.08	4.47	4.56	10.4	3.1	1615	1310	530	320	
$[NiL_2(I.Q)_2]$	8.89	9.08	4.45	4.56	14.3	3.2	1630	1320	530	320	11.5(7). 26(16), 15(6).
$[NiL_2(2,6\text{-Lut})_2]$	9.77	9.93	4.62	4.74	15.0	3.0	1620	1315	510	320	10(6),14.5(5.5) 24.5(15).
$[NiL_2\,en]$	13.28	13.43	6.25	6.40	11.4	2.9	1610	1310	520	330	11.5(8), 17(7), 28(17).

L = Ethyl malonate, Py = Pyridine, γ-Pic = 4-Methyl pyridine, Pip = Piperidine, Q = Quinoline, I.Q. = Isoquinoline, 2, 6-Lut = 2, 6-Lutidine, en = ethylenediamine.

15-17, and 24-28 K.K. region assignable[4] to $3A_{2g} \rightarrow 3T_{2g}$, $3A_{2g} \rightarrow 3T_{1g}(F)$ and $3A_{2g} \rightarrow 3T_{1g}(P)$ transition respectively. Extinction coefficient values are low in conformity with octahedral environment. Comparison of the bands with the solid state reflectance spectra of one representative compound indicates a little dissociation of the ligands inspite of the added base as the bands in solution spectra are at lower energy. It is quite probable that there is a distortion of the octahedron in solution as the two nitrogen ligands are in transposition. Hence the complexes have presumably a spin-free octahedral configuration on the basis of their a nalysis, magnetic moments and electronic spectral data.

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Mercury Complexes of Sulphonamides

G. S. Misra and M. V. Ramakrishna Rao

Department of Post-Graduate Studies and Research in Chemistry, University of Jabalpur, Jabalpur(M.P.)

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Misra *et al*[1-3] and Shukla *et al*[4] have reported the cyanoethylation of a large number of sulphonamides. Such cyanoethylated compounds form complexes with mercuric ion with great facility[5]. Recently sulphonamides were used as a complexing agent for various metals[6] and it was shown by bacteriostatic studies that these complexes are more potent than the parent drugs[7].

The present communication deals with the study of complexes of some more substituted sulphonamides and cyanoethylated sulphonamides with mercury (II) chloride.

Experimental

Preparation of complexes :

The cyanoethylated sulphanilamides were prepared according to the method of Misra *et al*[3].

All the complexes reported were prepared by refluxing a calculated amount of the sulphonamide and mercuric chloride in absolute alcohol. An alcoholic solution of sodium hydroxide was added to the refluxing mixture until the *p*H remained constant at approx. 8. Refluxing was continued for 2-3 hr. The product obtained was filtered, washed several times with alcohol and dried in a vacuum desiccator.

The quantitative estimation of mercury, chlorine and sulphur was done by the usual methods, viz., mercury volumetrically by titration with thiocyanate[8], chlorine gravimetrically as AgCl and sulphur gravimetrically as $BaSO_4$. Conductivity measurements were carried out in nitrobenzene with a conductivity bridge (Philips). Infrared spectra (KBr) were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer (Model-177). The results of the chemical analysis are given in Table 1.

Results and Discussion

All the complexes were quite stable and were found to be insoluble in most of the common organic solvents, viz., benzene, diethyl ether, carbon tetrachloride, chloroform and acetone. They are sparingly soluble in nitrobenzene. The analytical results reveal that the ligand and metal are in equimolecular ratio (1 : 1). The low molar conductance shows that these complexes are non-electrolytic in nature[9]. The non-electrolytic natnre of the complexes shows that the halogen atoms are also bonded to mercury with its inner coordination sphere. This gives coordination number four in all the complexes.

The infrared spectra of the ligand as well as their complexes have been examined. Only the important sites in the sulphanilamide and cyanoethylated sulphanilamide, viz.,—NH—and—C≡N groups have been taken into account.

—NH— of the sulphanilamide has two sharp bands at 3380 and 3480 cm^{-1} owing to the symmetric and N—H stretching vibrations. These bands of —NH— group shift to a lower frequency region in the complexes. As both the $—NH_2$ groups in the sulphanilamide molecule have a lone pair of electrons, it may be concluded the two NH_2 groups are attached to the two mercury giving a dimeric species, which also explains the insolubility of the complex. A tentative structure of the complex is given in Fig. 1.

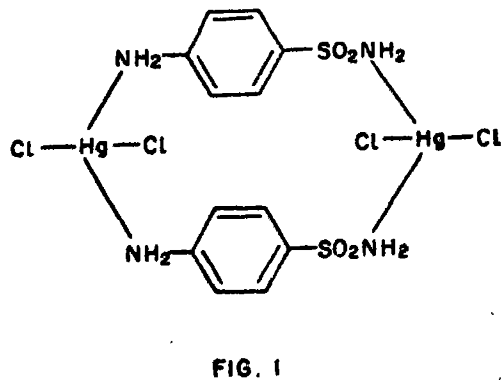


FIG. 1

TABLE 1 EXPERIMENTAL DATA OF MERCURY COMPEXES OF SUBSTITUTED SULPHONAMIDES

Serial No.	Compunds	% Merury Found (Calcd.)	% Chlorine Found (Calcd.)	% Sulper Found (Calcd.)
1.	Dichloro-(sulphanilamide) mercury II	45.50 (45.23)	16.00 (16.01)	7.20 (7.21)
2.	Dichloro-(sulphapyridine) mercury II	38.51 (38.48)	13.20 (13.61)	6.60 (6.14)
3.	Dichloro-(sulphathiazole) mercury II	37.74 (38.09)	12.99 (13.48)	12.50 (12.15)
4.	Dichloro-(sulphadiazine) mercury II	38.70 (38.48)	14.14 (13.61)	6.00 (6.14)
5.	Dichloro-(sulphamerazine) mercury II	37.78 (38.31)	13.48 (13.56)	6.00 (6.11)
6.	Dichloro-(sulphadimidine) mercury II	35.96 (36.42)	12.49 (12.89)	6.01 (5.81)
7.	Dichloro-(cyanoethyl sulphanilamide) mercury II	36.04 (36.5.)	13.00 (12.92)	5.10 (5.74)
8.	Dichloro-(cyanoethyl sulphapyridine) mercury II	34.75 (34.90)	12.64 (12.36)	6.01 (5.57)
9.	Dichloro-(cyanoethyl sulphathlazole) mercury II	34.23 (34.60)	12.50 (12.25)	11.60 (11.04)
10.	Dichloro-(cyanoethyl sulphadiazine) mercury II	35.20 (34.90)	12.50 (12.36)	5.10 (5.57)
11.	Dichloro-(cyanoethyl sulphamerazine) mercury II	35.01 (34.78)	12.62 (12.34)	6.10 (5.55)
12.	Dichloro-(cyanoethyl sulphadimidine) mercury II	33.50 (33.29)	12.30 (11.79)	5.79 (5.31)

In the cyanoethylated sulphanilamide, the band observed at 2260 cm^{-1} corresponds to the —C≡N stretching band. The bands at 3380 and 3500 cm^{-1} are due to the —NH— group. In the complex, these bands due to—C≡N as well as —NH— group shift to a lower frequency which may be attributed to the coordination effect. A dimeric species, as in the case of sulphanilamide, can be postulated to be existing in cyanoethylated sulphanilamide. A plausible structure for the complex has been put forward in Fig. 2.

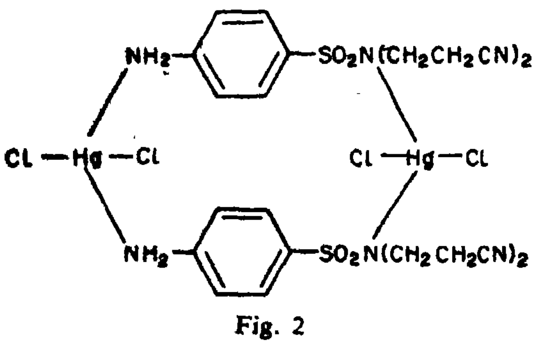


Fig. 2

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Kinetics and Mechanism of Reduction of Tris(acetylacetonato)-cobalt(III) by Hydroxylamine and Formate in Acid Media

A. K. BASAK and D. BANERJEA*

Inorganic Chemistry Laboratories, Department of Chemistry, University College of Science,
92, Acharya Prafulla Chandra Road, Calcutta-700009, INDIA.

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The kinetics of reduction of tris(acetylacetonato)cobalt(III) by hydroxylamine and formate in aqueous acid media have been studied spectrophotometrically under different conditions. Both the complex and its protonated form are reduced by the reductants with specific rate constants k_R and $k_{H,R}$ respectively which are concurrent to the acid catalysed self reduction of the complex. From detailed analysis of the effects of acid and reductant concentrations on the rate of reduction the specific rate constants for the different paths at different temperatures and the corresponding activation parameters have been evaluated at an ionic strength of 2*M*. Evidence has been presented in favour of a sort of inner-sphere mechanism of reduction involving formation of a H-bonded intermediate followed by its redox transformation by a H-atom transfer mechanism.

KINETIC studies on the reduction of tris(acetylacetonato)cobalt(III) by hydrazine in acid media have been reported earlier[1]. The results seem to indicate that the reduction occurs through the formation of an intermediate in which the reductant is hydrogen bonded to the oxygen of the chelated acetylacetonate ligand, followed by its transformation into the primary products of the redox reaction by a H-atom transfer process. Based on studies on the kinetics of reduction of this cobalt complex by hydroxylamine and formate in acid media and comparison of the behavior of these systems with those containing tris(oxalato)cobaltate(III) ion as the oxidant in place of $Co(acac)_3$, further evidence has been obtained in support of this inner-sphere type of reduction mechanism.

Experimental

Materials and Reagents :

The cobalt complex was prepared as reported earlier[2]. Hydroxylamine hydrochloride, $NH_2OH.HCl$ (A.R., B.D.H.) was purified by recrystallisation from aqueous ethanol. An aqueous solution of this was standardised oxidimetrically[3] using $KBrO_3$ every time before use. Pure sodium formate (E. Merck) was recrystallised twice from water and its purity was checked oxidimetrically[4] with $KMnO_4$. All other chemicals used were purified by usual methods before use.

Experimental procedure for the measurement of rate was the same as described earlier[1]. Only in the case of hydroxylamine the reactions were studied in HCl-KCl media, while in the case of formate $HClO_4$-$NaClO_4$ media was used as in earlier work[1]. This was necessary in view of the unstable nature of hydroxylamine perchlorate systems. From the known basicity constants of hydroxylamine[5] and formate[6] it followed that the reductants were virtually completely present in their protonated forms ($^+NH_3OH$ and HCOOH) in the range of acid and reductant concentrations used in the experiments.

Results and Discussion

As in the case of reduction by hydrazine a three term rate law was observed in each case :

$$k_{obs} = k_H[H^+] + \{k_R + k_{H,R}[H^+]\}[R]$$

where k_{obs} is the experimentally determined pseudo-first-order rate constant for the reduction of the cobalt(III) species under a particular set of conditions in presence of excess of H^+ and the reductant, while k_H, k_R and $k_{H,R}$ are the specific rate constants for the acid catalysed self-reduction of $Co(acac)_3$, reduction of $Co(acac)_3$ by the reductant (R) and reduction of the protonated form of $Co(acac)_3$ by the reductant respectively ($R = {}^+NH_3OH$ or HCOOH as the case may be). Values of these rate constants were evaluated graphically as described earlier[1] are given in Table 1.

The value of the rate constant k_H obtained from experiments in perchloric acid medium in presence of formate is the same (within limits of experimental error) as that obtained earlier from the investigations using hydrazine as the reductant[1], as is to be expected.

For reduction by hydroxylamine measurements were made in aqueous HCl-KCl media because of the unstable chemical nature of hydroxylamine-

* Senior author to whom all correspondence to be made.

TABLE—1. VALUES OF KINETIC PARAMETERS
(IONIC STRENGTH, 2M)

Reductant	Temp. °C	$10^4 k^*_{H(Cl)}$, M^{-1} sec^{-1}	$10^4 k_R$, M^{-1} sec^{-1}	$10^5 k_{H,R}$ M^{-2} sec^{-1}
Hydroxylamine	40	0.61	0.51	1.83
	50	3.55**	2.25	8.25
	60	18.05	8.00	33.48
$\Delta H^{\neq}$, kcal mole^{-1},		35.0	27.9	32.7
$\Delta S^{\neq}$, e.u.,		28.9	5.9	28.2
		$10^6 k_H$, M^{-1} sec^{-1}	$10^6 k_R$, M^{-1} sec^{-1}	$10^6 k_{H,R}$ M^{-2} sec^{-1}
Formate	35	1.64	0.58	2.04
	40	3.93	1.83	3.78
	45	7.94	5.21	6.82
	50	16.37	14.30	11.35
$\Delta H^{\neq}$, k cal. mole^{-1}.,		30.1	42.0	21.6
$\Delta S^{\neq}$, e.u.,		16.9	53.4	−10.3

* See text.

** k_H value obtained directly from decomposition of $Co(acac)_3$ in HCl-KCl media (μ, 2M) at 50° in absence of an external reductant is $3.57 \times 10^{-4} M^{-1} sec^{-1}$. This is significantly lower than that obtained in $HClO_4$-$NaClO_4$ media for which the value is $17.5 \times 10^{-4} M^{-1} sec^{-1}$ at μ, 2M($8.8 \times 10^{-4} M^{-1} sec^{-1}$, at μ, 1M)[7]. Hence, k_H in HCl-KCl media is denoted as $k_{H(Cl)}$.

perchloric acid system. In this case the k_H value obtained was significantly less than that obtained in perchloric acid media. However, this lower k_H value was found to be identical to that obtained from studies on the decomposition of the complex itself in HCl-KCl media in absence of any external reductant, while the higher k_H value observed in other two cases in perchloric acid media was identical to the value observed from studies on the decomposition of the complex in $HClO_4$ media[7] in absence of any external reductant. It is significant to note in this connection the observation of Haight, Jr., et.al.[8] that the rate of reduction of chromium(VI) by hydroxylamine is significantly less (a factor of ca. 6 under their experimental conditions) in HCl than in $HClO_4$ media. This is obviously because $HClO_4$ is a better proton donor than HCl as is apparent from the H_0 values[9] and the dissociation constants[10(a,b)] of the two acids (at 25°, μ=0, $HClO_4$ is *ca.* 5.5 times stronger than HCl for solutions of the two acids of the same molar concentrations). Accordingly, the neutral substrate $Co(acac)_3$ will be more protonated in $HClO_4$ than in HCl solution of the same molar concentration of the acids, thus causing a faster overall decomposition in $HClO_4$ than in HCl of the same molar concentration, leading to a higher value of k_H in $HClO_4$ than in HCl. Hence for differentiating the experimental k_H value in HCl media it has been denoted as $k_{H(Cl)}$ in Table 1.

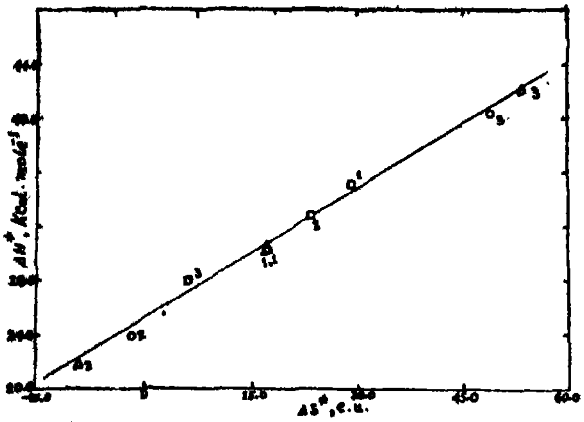


Fig. 1. Isokinetic relationship: Plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ for different systems corresponding to different reaction paths (Ionic strength, 2M).

○ : $Co(acac)_3$-Hydrazine in perchlorate media.
△ : $Co(acac)_3$-Formate in perchlorate media.
□ : $Co(acac)_3$-Hydroxylamine in chloride media.
1 : Values corresponding to k_H.
2 : Values corresponding to $k_{H,R}$.
3 : Values corresponding to k_R.

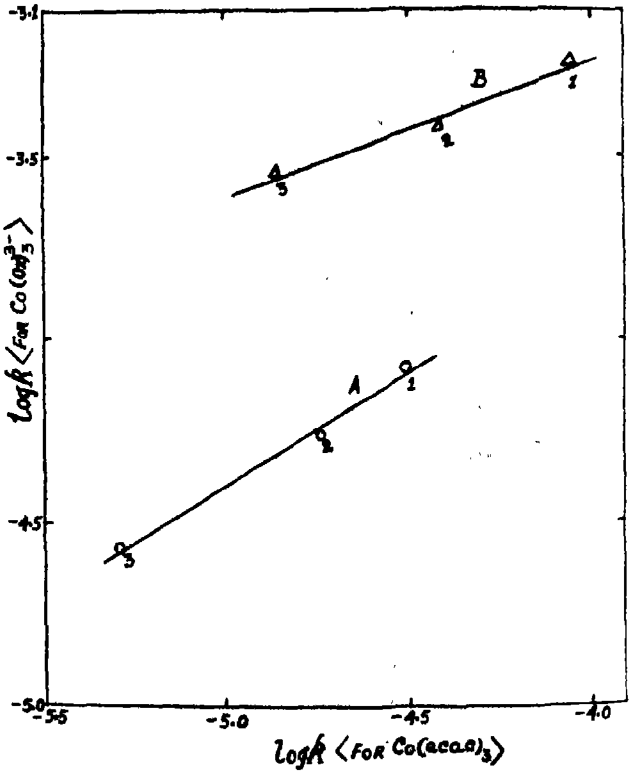


Fig. 2. Log-log plot for correlating the specific rates of oxidation of hydrazine, formate and hydroxylamine by tris-(oxalato)cobaltate(III) ion and tris(acetylacetonato)-cobalt(III). (Temp., 40°; Ionic Strength, 2M).
A : $k=k_R$; B : $k=k_{H,R}$.
1 : Hydrazine, 2 : Formate,
3 : Hydroxylamine.

The plot of ΔH^* vs ΔS^* for all the different rate constants and the three different reductants (viz. $N_2H_5^+$, $^+NH_3OH$ and HCOOH) is linear (see Fig. 1) and this isokinetic relationship[11] suggests that similar mechanism of reduction operates in all the cases, i.e. for the different reaction paths and the different reaction systems studied. Similar investigations have also been made[12] on the reduction of $Co(C_2O_4)_3^{3-}$ by the three different reductants and comparison of the behaviour of the two oxidant systems also furnishes additional useful mechanistic information. Thus, it has been observed that both for k_R and $k_{H,R}$ the log-log plot of the rate constants of the two systems is linear with a slope much different from unity (see Fig.2) which is indicative[13] of some sort of inner-sphere mechanism of the type suggested earlier.

In the case of $^+NH_3OH$ and HCOOH the primary oxidation products of these reductants resulting from the hydrogen atom transfer mechanism of reduction of the cobalt(III) complex[1] would be the radical species $\cdot ONH_3^+$ (or possibly $\cdot ONH_2+H^+$)[8] and $HCOO\cdot$[14(a,b)], respectively. The former is known to decompose very rapidly[8] forming N_2 while the latter is likely to react with the cobalt(III) species in a fast step leading to Co(II) and CO_2.

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Kinetics of Mercuration of *o*-, *m*- and *p*-hydroxy Benzoato-pentaammine Cobalt(III) Complexes

(Mrs) NIVEDITA MULLICK and R. K. NANDA*

Department of Chemistry, Utkal University, Bhubaneswar-4.

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The kinetics of mercuration of *o*-, *m*- and *p*-hydroxy benzoato pentaammine Co(III) perchlorate in aqueous perchloric acid have been studied using $Hg(ClO_4)_2$ as the mercurating agent. The second order rate constants are found to be independent of $HClO_4$ concentration within the range 0.10-0.25*M*. The average value of the rate constants at 40° for the *o*-, *m*- and *p*-hydroxy benzoato complexes and the activation energ (E_A) for the reaction are found to be 3.5×10^{-4} sec^{-1}M^{-1} (13.4 K.cal/mole), 3.0×10^{-4} sec^{-1} M^{-1} (12.3 K. cal/mole) and 2.0×10^{-4} sec^{-1} M^{-1} (10.2 K. cal/mole) respectively.

AROMATIC ligands, with donor functions suitably situated in the aromatic system, on co-ordination to metal ions could, in principle, provide a number of systems in which the change in the reactivity of the aromatic ring towards electrophilic reagents on co-ordination to metal ions could be conveniently examined. The rates of iodination of 8-quinolinol and its derivatives[1,2] have been reported to be significantly reduced, compared to the free ligand anions, in the presence of several metal ions. Similar observations have been made in the kinetic study of the diazo coupling of the Zn(II) chelate of 8-quinolinol-5-sulphonic acid[3] and the mercuration of the Cu(II) chelate of 8-quinolinol[4]. With labile complexes of the type cited above it is rarely possible to interpret the rate data unequivocally in terms of the reactivity of the ligand which remains co-ordinated to the metal ion during the entire course of the reaction. Jones et.al[5] have reported that the rate of bromination of aniline in $[Co(en)_2$ (Aniline) $Cl]^{2+}$ or $[Co(en)_2(aniline)(OH_2)]^{3+}$ is retarded by a factor of 10^{10} as compared to free aniline. Gillard, Houghton and Tucker[6] have also reported that 1,10-phenanthroline when co-ordinated to Rh(III) or Co(III) undergoes nitration at a faster rate as compared to the free ligand under comparable conditions. In the present paper the kinetics of the mercuration reaction of *o*-hydroxy-, *m*-hydroxy and *p*-hydroxy benzoatopentaammine cobalt(III) complexes in aqueous perchloric acid solution using Hg(II) perchlorate as the mercurating reagent are reported. These constitute a system of inert complexes from which the release of the phenolic acids[7] are known to take place too slowly to complicate interpretation of the rate data in any way. Since Hg^{++} is known to be the attacking agent in aromatic mercuration[8], mercuric perchlorate in aqueous perchloric acid, as used in the present investigation, would be expected to be a superior mercurating agent[9]. Hg(II) perchlorate in dilute aqueous solution may be assumed to be fully ionised and as such, its use as the mercurating agent would be expected to simplify the form of the rate expression.

Experimental

The hydroxy benzoatopentaammine cobalt(III) perchlorates were prepared by the method of Gould and Taube[10]. The purity of the complexes were checked by estimating their Co content[11]. Anal. Calc. for $[(NH_3)_5CO$ (*o*-hydroxy benzoato)$]$ $(ClO_4)_2$(I) : Co, 12.28. Found : Co, 12.40 ; $[(NH_3)_5$ Co(*m*-hydroxy benzoato)$]$ $(ClO_4)_2$(II) : Co, 12,28. Found : Co, 12.07 ; $[(NH_3)_5$Co (*p*-hydroxy benzoato)$]$ $(ClO_4)_2$(III) : Co, 12.28. Found : Co, 12.0.

Mercuric perchlorate solution was prepared by dissolving weighed amount of yellow mercuric oxide (G.R, E.M) in slightly more than the stoichiometric amount of 70% $HClO_4$ (G.R, E.M). The mixture was warmed over a steam bath for 2 hours, allowed to cool to the room temperature and filtered. Hg content of the stock solution was estimated by E.D.T.A. titration using Erio-T indicator[12]. In order to determine the free perchloric acid in the stock $Hg(ClO_4)_2$ solution, to a known volume of the solution was added excess of Dowex 50×8 cation exchange resin in the acid form. After allowing for the exchange to be complete, the solid particles were filtered on a bed of glass wool and washed quantitatively with distilled water. The total acid in the filtrate was estimated by titration against standard alkali. Hg^{++} content of the solution being known, the free acid could be calculated.

All other reagents used were of B.D.H., A.R quality. Double distilled water was used for preparing all reagent solutions.

For measuring the rate of mercuration of the substrates, a weighed amount of the complex was transferred into a 5 ml volumetric flask containing calculated amounts of $HClO_4$ and $NaClO_4$ (to adjust the ionic strength). The contents were allowed to equilibrate inside a water thermostat maintained at a definite temperature. $Hg(ClO_4)_2$ solution of appropriate concentration was also allowed to equilibrate at the same temperature. After thermal equilibrium was attained, a definite volume of the $Hg(ClO_4)_2$ solution was quickly transferred into the reaction flask and the timer was started. The volume was made up with distilled water equilibrated at the same temperature, the contents were well-shaken and the reaction flask was quickly replaced inside the thermostat. 5.0 ml aliquots were withdrawn at preset time intervals and run into conical flasks containing 5.0 ml of 1*M* NaCl solution so as to quench the reaction. Excess $HClO_4$ in the mixture was neutralised with a few drops of 0.5*M* NaOH and then diluted with about 30 ml of distilled water. Sufficient EDTA (0.01*M*) solution so as to be in slight excess was run in, followed by 2.0 ml of a NH_4Cl - NH_4OH buffer ($pH = 10$). Excess EDTA was back titrated with 0.01*M* $ZnSO_4$ solution using Erio-T indicator. EDTA is known to react[13] only with the free $HgCl_2$. The concentration of the unreacted Hg(II) at different time intervals, was, therefore, computed from the volume of $ZnSO_4$ consumed.

Results and Discussion

The kinetics of mercuration of all the three complexes has been carried out at 35, 40 and 45° and at an ionic strength of 0.3*M*. The concentration of the complex and $Hg(ClO_4)_2$ was kept fixed at $5.0 \times 10^{-3} M$ for all the runs. $HClO_4$ concentration in the reaction mixture was varied within 0.10-0.25*M*. Kinetic runs at lower acidities were not undertaken in order to avoid the hydrolysis of $Hg(ClO_4)_2$. The concentration of free $HClO_4$ present in $Hg(ClO_4)_2$ was taken into account in calculating the total $[H^+]$ of the reaction mixtures. The rate constants (k_{obs}) for the mercuration reaction of the substrates were calculated from reasonably good second order plots. The 'k_{obs}' values for the *o*-, *m*- and *p*-hydroxy benzoatopentaammine Co(III) complexes at different temperatures and $[HClO_4]$ are collected in Table 1. The activation energies (E_A) for the mercuration reaction of the complexes were calculated from the slopes of the plot of log k_{obs} *vs* 1/T. The 'E_A' values for each of the complexes are collected in Table 1.

The overall reaction for the mercuration of these substrates may be expressed as :

$$[(NH_3)_5CoO_2CC_6H_4(OH)]^{2+} + Hg(ClO_4)_2 \rightleftharpoons [(NH_3)_5Co\,O_2C\,C_6H_3(OH)(HgClO_4)]^{2+} + H^+ + ClO_4^- \quad \ldots(1)$$

Jones et. al[4] obtained evidence for multiple mercuration (two-Hg Acetate in one ring and one-Hg Acetate in the other) of the bis-chelate of 8-hydroxy quinoline Cu(II) complex in the course of their preparative experiments. In the present experiments the mercuration kinetics was followed up to 50-60% reaction in each case. The second order rate constants were calculated on the assumption that the mercuration reaction of these substrates were first order with respect to the complex and first order with respect to $Hg(ClO_4)_2$. The fact that good straight line plots were obtained which yielded reasonably constant values of 'k_{obs}' leads us to believe that the reactions proceed in accordance with Eq(1) and therefore, multiple mercuration does not take place under these experimental conditions.

TABLE—1

KINETICS OF MERCURATION OF HYDROXY BENZOATO-PENTAAMMINE COBALT(III) PERCHLORATES

[Complex] = 5.0×10^{-3}M, $[Hg(ClO_4)_2]$ = 5.0×10^{-3}M, Ionic strength = 0.3M

$[HClO_4]$, M	$10^3 k_{obs}$ Sec^{-1} M^{-1} 35°C	40°C	45°C	50°C	EA, K.cal/mole
Complex : $[(NH_3)_5Co(o\text{-hydroxy benzoato})](ClO_4)_2$					
0.10	2.8	3.5	5.9	—	
0.15	3.1	3.5	5.3	—	13.4
0.20	2.8	3.5	5.7	—	
0.25	2.7	—	—	—	
Complex : $[(NH_3)_5Co(m\text{-hydroxy benzoato})](ClO_4)_2$					
0.10	2.5	2.9	4.2	—	
0.15	2.2	3.1	4.5	—	
0.20	2.4	3.1	4.6	—	12.0
0.25	2.5	—	4.1		
Complex : $[(NH_3)_5Co(p\text{-hydroxy benzoato})](ClO_4)_2$					
0.10	—	2.3	2.8	3.8	
0.15	—	2.3	2.6	3.8	10.2
0.20	—	2.3	2.6	3.8	

The second order rate constants for all the three substrates are seen to be practically independent of $[H^+]$ within the range 0.10 to 0.25*M*. This indicates that the reverse reaction (Eq.1) is not kinetically significant under the present experimental conditions. The electrophilic substitution reactions of phenols have generally been interpreted in terms of the reactivity of the phenol and the phenate species The dissociation constant of the phenolic group o. *o*-, *m*- and *p*- hydroxy benzoato pentaammine Co(IIIf complexes have been found to be 5.1×10^{-12}) 2.8×10^{-10}, and 4.3×10^{-10} respectively at 30°[14]. In view of the very low dissociation constants of the phenolic group of these substrates, at the $[H^+]$ at which the present investigation has been carried out, the phenol form of the substrate would be expected to be the only reactive species. The independence of the 'k_{obs}' values of $[H^+]$ is in accordance with this assumption. Further, the acid independence of the second order rate constants for the mercuration reaction of these substrates indicate that the ligands remain co-ordinated to the $(NH_3)_5Co(III)$ centre during the course of the reaction.

The activation energy (E_A) for the mercuration reaction of the *o*-, *m*- and *p*-hydroxy benzoato complexes have been found to be 13.4, 12.0 and 10.2 K. cal/mole respectively. The activation energy for the mercuration of the bis-Cu(II) chelate of 8-hydroxy quinoline by mercuric acetate in glacial acetic acid has been reported to be 10 K.cal/mole[4] and that for the mercuration of benzene and toluene under similar experimental conditions to be 21 K.cal/mole[15]. These values, though close to the results obtained in the present investigation, are not strictly comparable since different mercurating agents and different media have been used. Comparison of the activation energy data reported in this paper with those of the corresponding free ligands would have been more meaningful, but these could not be determined due to the low solubility of the Hg(II) salts of these hydroxy benzoic acids.

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Enthalpies and Free Energies of Solvation of Sodium and Potassium Chlorides in Dimethyl Sulphoxide at 25°

A. K. R. UNNI*, N. SITARAMAN and V. K. C. MENON

Chemistry Department, Regional Engineering College, Calicut, Kerala.-673601.

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The solubilities of NaCl and KCl have been measured in DMSO in the temp. range 25°-95°. The solubilities increase slightly with temp. The enthalpies and free energies of solution and solvation have been calculated. Enthalpies and free energies of solvation of the electrolytes are plotted against $\frac{1}{r_+ + \delta}$. The individual ionic contributions obtained from the graph agree closely with these calculated from the modified Born equation. The adjustable parameter $\delta = 0.845$ Å for cations and 0.39 Å for anions.

EVEN though much work has been done on the solvation of alkali halides in non-aqueous solvents like Formamide, NMF, DMF, CH_3CN, etc.[1,2] little work seems to have been done on the solvation of sodium and potassium chlorides in DMSO. As the salts are not easily soluble, calorimetric measurements of the enthalpies of solvation are difficult and hence not attempted. The only other alternative is to get these from solubility data. Strangely enough only very little information is available on the solubility of these salts in DMSO and the data are not in agreement.[3,4] An attempt is made in the present work to check the solubilities reported and to arrive at the enthalpies and free energies of solvation from solubility measurements.

Experimental

DMSO (B.D.H.) was purified by vac. fractionation.[5] The middle fraction was repeatedly fractionated. The water content of the final product was estimated by Karl Fischer titration. It was found to be 0.001%. The physical constants at 25° were : m.p., 18.55° ; d., 1.095g cm^{-3} ; Sp. cond., 2-3 $\times 10^{-8}$ mho cm^{-1}.

Sodium and potassium chlorides (Merck.G.R.) were recrystallised twice from conductivity water and dried at 110° in vac. for several hours. The purity of the salts was determined gravimetrically ; the purity was found to be NaCl 99.97±0.01% and KCl 99.98±0.01%.

Saturated solutions were prepared by the method given by A. J. Parker[6]. Solvent and the solutions were handled in a dry box. As DMSO is highly hygroscopic all precautions were taken to exclude moisture at every stage. Temperature was maintained in a thermostat within ±0.01°. Weighed quantities of the solutions were analysed gravimetrically both for the metal and for the chloride. Solubilities were calculated in g.per 100 g. of the solvent and as moles per Kg. of the solvent.

Results and Discussion

The solubilities of both the salts increase linearly with temperature. At all temperatures the solubility of KCl is less than that of NaCl. Solubilities of the salts at different temperatures are given in Table 1. The solubilities at 25° obtained in the present work agree well with these reported by C.A. Melendres[4], but differ from those of Kenttamaa[3].

TABLE 1—SOLUBILITIES OF NaCl AND KCl IN DMSO AT DIFFERENT TEMPERATURES (G/100 G. OF THE SOLVENT)

Salts	25°	40°	50°	60°	70°	80°	94°
NaCl	0.455	0.465	0.472	0.478	0.485	0.491	0.501
KCl	0.168	0.174	0.178	0.183	0.187	0.191	0.197

$H^\circ_{(sat)}$ at 25° were calculated from the slope of log S *vs* $\frac{1}{T}$ graph. The plots are linear for both the salts in the temperature range studied showing that $\Delta H^\circ_{(sat)}$ is practicallyc onstant. The values are +0.30 and +0.511 K.cal. $mole^{-1}$ for NaCl and KCl respectively. Though these values of $\Delta H^\circ_{(sat)}$ may be different from the usual calorimetric ΔH° values, it is assumed that there will not be much change in these values due to heat of dilution since ion pair formation is reported to be negligible in DMSO[7]. Therefore values of enthalpies of solvation based on these $\Delta H^\circ_{(sat)}$ values may be only slightly in error.

The enthalpies of solvation of the salts are calculated from $\Delta H^\circ_{(sat)}$ and the lattice energies[8] of these salts. According to the modified Born equation a plot of these enthalpies against $\frac{1}{r_+ + \delta}$ (r_+ is

the crystallographic radii of the cations and δ the adjustable parameter) should be a straight line for a closely related series of salts with a common anion.

The enthalpies of solvation of the salts LiCl[9], NaCl and KCl are plotted against $\frac{1}{r_+ + \delta}$ of positive ions. A value of $\delta = 0.845$ Å gave the best fitting straight line. The intercept of this line gives the enthalpy of solvation of the common anion–chloride (Fig. 1). The enthalpies of solvation of K^+ and Na^+ were calculated using this value. The enthalpy contribution of K^+ was also determined independently from a plot of the enthalpies of

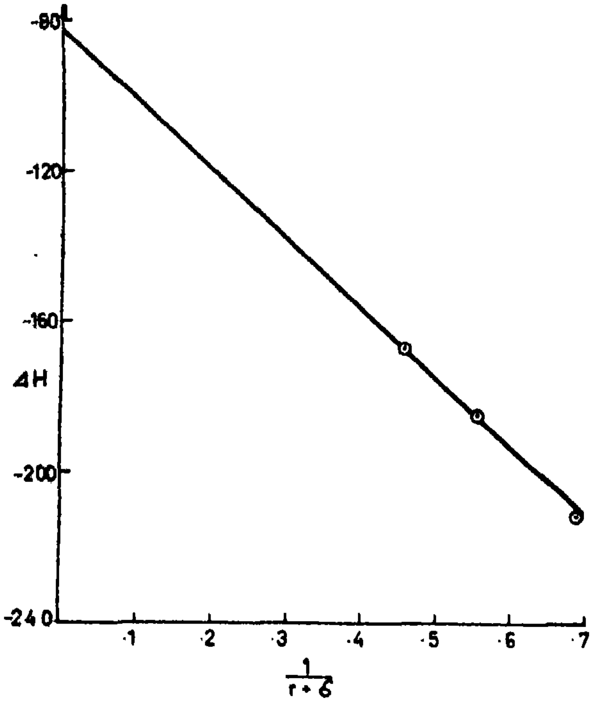


Fig. 1

solvation of KCl, KBr and KI *vs* $\frac{1}{r_- + \delta}$ of the anions ($\delta = 0.39$ Å)

The ionic enthalpies of solvation in DMSO were also calculated using the enthalpies of solvation of these ions in water and the enthalpies of transfer from water to DMSO reported by Arnett and McKelvey[10]. The agreement is found to be good.

The free energies of solvation are calculated from the solubility data.

$-\Delta G^\circ = 2 \times 2.303\ RT \log (m\, \gamma\pm)$ where m is the solubility in moles Kg^{-1} and $\gamma\pm$ the mean molal activity coefficient of the electrolyte in the saturated solution. $\gamma\pm$ of NaCl is obtained by the authors from freezing point depression measurements. In the case of KCl $\gamma\pm$ is calculated from Debye-Hückel limiting law. From the free energies of solution, the standard free energies of formation in the solvent and the free energies of solvation of the electrolytes are calculated by the method given by Criss and Luksha[11].

The free energies of solvation of the individual ions were determined graphically as in the case of enthalpies of solvation. These agree with those calculated from the modified Born equation.

The enthalpies and free energies of solvation of the salts are given in Table 2 and those of the ions in Table 3.

The free energies and enthalpies of solvation of the cations are more negative in DMSO than in water. This indicates that DMSO is a better solvating medium for the alkali ions. The enthalpies and free energies of solvation increase in the order $K^+ > Na^+ > Li^+$. On the other hand, the enthalpies and free energies of solvation of Cl^- are more positive than in water showing that the ion is less solvated. In DMSO, the centre of anion solvation is the S atom of the S–O dipole. This is sterically shielded by

TABLE 2—ENTHALPIES AND FREE ENERGIES OF SOLVATION OF LiCl, NaCl & KCl at 25° (K. cals mole^{-1})

Salt	$\Delta H^\circ_{(sat)}$	Lattice energy	$\Delta H^\circ_{(solv)}$	$\Delta G^\circ_{(solv)}$	$\Delta G^\circ_{(solv)}$	$\Delta G^\circ_{(calc)}$
LiCl	−10.9 ± .3	−203.4	−214.3 ± .3	—	—	—
NaCl	+ 0.303	−185.8	−185.5	+3.58	−164.4	−164.48
KCl	+0.511	−168.9	−168.4	+4.93	−146.7	−148.65

TABLE 3—ENTHALPIES AND FREE ENERGIES OF SOLVATION OF Li^+, Na^+, K^+ and Cl^- at 25° (K. cal.mole^{-1})

Ion	Radius Å (Pauling)	$\Delta H^\circ_{(solv)}$	$\Delta H^\circ_{(solv)}$ (calc. from enthalpies of transfer)	$\Delta G^\circ_{(solv)}$	$\Delta G^\circ_{(solv)}$ (Calc)
Li^+	0.60	−130.8	—	—	—
Na^+	0.95	−102.0	−101.75	−90.4	−90.57
K^+	1.33	− 85.0	− 84.64	−72.7	−74.74
Cl^{-1}	1.81	− 83.5	− 83.87	−74.0	−73.91

the two methyl groups. Moreover charge density (+) of the S atom is decreased by the inductive effect of the two methyl groups. These combined effects seem to reduce the anion solvation. If anion solvation is the decisive factor in determining the relative solubilities in protic and dipolar aprotic solvents the lower solubilities of these salts in DMSO may be well explained by the low anion solvation existing in this solvent.

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New Baths for the Deposition of Manganese and Cobalt Oxides

M. M. ELSEMONGY, M. M. A. GOUDA and Y. A. ELEWADY

Chemistry Department, Faculty of Science, Mansoura University, Egypt.

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New methods have been adopted for the anodic deposition of the different manganese and cobalt oxides. The deposition of the different oxides is usually carried out from their metal salt solutions in presence of a complexing agent or a reducing agent. The oxides deposited are as follows: Mn_2O_3 from manganous sulphate in presence of boric acid and formaldehyde at pH = 5.5, Mn_3O_4 from manganous sulphate in presence of formic acid at pH = 5.0, MnO from manganous sulphate-ammonium chloride solution in presence of telluric acid, Co_2O_3 from cobalt chloride in presence of telluric acid and sodium fluoride, Co_3O_4 from cobaltite in presence of formaldehyde and potassium chloride and finally CoO from cobalt chloride in presence of alcohol. The results of chemical analysis revealed that the purity of the oxides is 99.99% and their molecular formulae are $MnO_{1.5}$, $MnO_{1.33}$, MnO, $CoO_{1.5}$, $CoO_{1.33}$ and CoO respectively.

ANODIC formation of Mn^{+2} and Mn^{+3} was observed by Agladze and Kharabadze[1] during the polarization of manganese in sulphuric acid solutions of different concentration. Bellone[2] found that insoluble compounds of a lower state of oxidation than MnO_2 could be obtained by electrolysis in a solution of alkali metal halide. Grube and Feucht[3] studied anodic oxidation of a solution of cobaltite and detected the formation of CoO, Co_3O_4 and CoO_2 at low, medium and high potentials respectively. Wernicke[4] and Goehn and Glaser[5] obtained cobaltic oxide di-hydrate by electrolysis of a solution of potassium cobalti-tartarate in potash-lye and drying the product in vacuum,

In the present investigation some oxides of manganese and cobalt were prepared by electrodeposition from baths containing the metal salt in presence of a complexing or a reducing agent.

Experimental

Materials and Apparatus

Standard solutions of manganous sulphate and cobaltous chloride were prepared from analar materials dissolved in double distilled water and their concentrations determined as described in Vogel[6]. Other materials used such as ammonium chloride, ammonium sulphate, boric acid, telluric acid, formic acid, formaldehyde, sodium carbonate, sodium fluoride and potassium chloride were prepared by dissolving the appropriate amount of A.R. or recrystallised material in double distilled water. For the electrodeposition of the different oxides an electrolytic cell with two compartments separated by a porous diaphragm was used. Each compart, is provided with a platinum wire. The electrolysing current was supplied from a 6- storage battery. Current regulation was mainta by a resistance box connected in series. It is t noted that in all the cases of electrodepositio the oxides of manganese and cobalt the bath t perature was maintained at 25°.

The Electrodeposition of Manganese and C Oxides

1—Mn_2O_3

The boric acid-formaldehyde bath : The electr was prepared by mixing 5 ml 0.99 *N* $MnSO_4$ solut 25 ml double distilled water, 5 gm NH_4Cl 0.302 gm boric acid. The solution was heatec dissolve the salts and after cooling 0.1 ml 6 *N* for dehyde solution was added. The acid solution then neutralised with 3.2 ml ammonia solution to $pH = 5.5$. The current density used amount 1 m.A./cm^2.

2—Mn_3O_4

The formic acid-ammonium sulphate bath : electrolyte was prepared by mixing 4 ml 0.9 $MnSO_4$ solution, 25 ml double distilled water, 0.1 6 *N* formaldehyde solution 10 gm ammon sulphate. The solution was boiled to dissolve salt and then neutralised with 4.5 ml ammon hydroxide to $pH = 5.0$. The current density amounts to 0.3 m.A./cm^2.

3—MnO

The formate-pyrogallol bath : The electr was prepared by mixing 5 ml 0.99 *N* $MnSO_4$ solut 25 ml distilled water and 5 gm ammonium chlo The solution was heated to dissolve the salt follo by adding 0.1 ml 6 *N* formaldehyde and 0.473 pyrogallol. The *p*H of the solution was maintai

at 3 using concentrated sulphuric acid. The current density used amounts to 1 m.A./cm^2.

4—Co_2O_3

The tellurate-sodium fluoride bath : The electrolyte was prepared by mixing 50 ml 0.15 *N* $CoCl_2$ solution, 1 gm telluric acid and 1 gm sodium fluoride. The current density used amounts to 1 m.A./cm^2.

5—Co_3O_4

The cobaltite-formaldehyde bath : In this case anodic deposition of Co_3O_4 was carried out from an electrolyte prepared by dissolving 13 gm NaOH in 20 ml 0.15 *M* $CoCl_2$ followed by adding 0.1 ml 6 *N* formaldehyde solution so that the final concentration of the alkali is 14.7 *M*.

To this solution 10 gm potassium chloride were added and the cobaltite solution heated to dissolve the salt. The current density applied amounts to 0.5 m.A./cm^2.

6—CoO

The sodium carbonate-alcohol bath : The electrolyte was prepared by mixing 50 ml 0.15 *N* $CoCl_2$ solution, 2 gm Na_2CO_3, 20 gm NaCl and 20 ml absolute alcohol. The current density applied was 0.5 m.A./cm^2.

Discussion

Mechanism of Oxide Formation

The formation of the different oxides studied is believed to take place as follows :

1—Mn_2O_3 : During the deposition of Mn_2O_3 oxide, the migration of the complex species, manganese borate $[Mn(B_4O_7)_2]^{-1}$ towards the anode occurs where it looses its charge and dissociates yielding Mn^{+3} or Mn^{+4} ions. These ions react with OH^{3-} ions forming Mn_2O_3.

2—Mn_3O_4 : The deposition of Mn_3O_4 oxide takes place by the migration of the $[Mn(CO_2H)_3]^{-1}$ species to the anode which on discharge and reaction with OH^- ions yields Mn_3O_4.

3—MnO : During the deposition of MnO from the formate-pyrogallol bath migration of $[Mn(CO_2H)_3]^{-1}$ species to the anode takes place. Direct discharge of the complex species takes place furnishing Mn^{+2} ions. These ionic species react with OH^- ions yielding the oxide.

4—Co_2O_3 : The deposition of Co_2O_3 from the tellurate bath is supposed to take place by the anodic migration of the ionic species $[Co(TeO_4)_3]^{-3}$, which looses its charge producing CoO^+ or Co^{+3} ions. These ions react with OH^- ions forming the oxide.

5—Co_3O_4 : The deposition of Co_3O_4 from the cobaltite bath takes place by the migration of $CoO_2^=$ species towards the anode, which on discharge yields CoO^+ or Co^{+3} ions and under the effect of the reducing agent produces Co_3O_4.

6—CoO : The deposition of CoO from the $CoCl_2$-alcohol takes place by the migration of the cobalt dialcoholate complex $[Co(EtO)_2]^{-1}$ towards the anode which on discharge yields Co^{+2} or Co^{+3} ions and under the effect of the reducing agent produces CoO.

The formation of Mn^{+3}, Mn^{+4} and Co^{+3} have been proved by Kharabadze and Grube[6,7] during the anodic oxidation of manganese or cobaltite.

From the literature of manganese complexes, Senet and Sanz[8] proved the structure of the manganic ditartarate complex as $[Mn(C_3H_2O)_2]^{-1}$. Similarly it is probable that a diborate complex exists. The formation of cobalt tellurate complex has been proved experimentally by heating cobaltous chloride with telluric acid in presence of H_2O_2, where a brown precipitate is formed. Similarly it is known that cobalt and manganese can form dialcoholate complexes.

The Effect of Complexing Agent/Metal Ion Ratio

Increase in the concentration of the complexing agent with Mn_2O_3 causes the deposition of a lower oxide due to the low concentration of the metal ions provided by the dissociation of the metal complex at the anode. On the other hand, increase of the metal ion/complexing agent ratio favours the deposition of a higher oxide.

The Effect of the Concentration of the Reducing Agent

The effect of the concentration of the reducing agents such as formaldehyde, or alcohol was studied during the deposition of Co_3O_4, MnO and CoO. Deposition of a higher oxide takes place in absence or at low concentration of the reducing agent. The role played by these reducing agents is attributed to their reducing properties on the higher oxidation products. The reducing power of formaldehyde increases with rise of *p*H and its concentration producing an oxide containing a high percentage of the lower oxide.

The Effect of pH

The effect of the *p*H of the bath on the oxide formed is quite important. Thus it has been observed that the optimum *p*H in the deposition of the oxides Mn_2O_3, Mn_3O_4 and Co_2O_3 is 5.0. A decrease in the *p*H of the solution assists the formation of a lower oxide presumably due to the relatively low concentration of OH^- ions discharged at the anode from acid solutions. On increasing the *p*H of the solution above 6, with Mn_2O_3 and Mn_3O_4 oxides, the percentage of the lower oxide also increases. This might be due to the increased reducing action of formaldehyde which becomes pronounced in alkaline medium. With Co_2O_3 increase in the *p*H from 5 to 7 exerts no effect on the oxide composition. On increasing the *p*H of the

solution, with CoO and MnO oxides, a higher oxide is deposited. The effect of alkalinity on the deposition of Co_3O_4 indicated that a higher oxide is deposited on increasing the alkalinity from 14.7-18.0N. A lower oxide is produced at relatively low alkalinities.

Effect of Some Added Salts

The effect of potassium chloride on the deposition of Co_3O_4 indicates that chloride ions assist the oxidation of the lower cobalt species which might be formed due to the reaction of the CoO_2^- with formaldehyde. Thus the decrease in the concentration of potassium chloride causes the formation of a lower oxide. The effect of sodium fluoride, sodium carbonate and pyrogallol on the deposition of Co_2O_3, CoO and MnO oxides indicates that these salts assist the formation of a coherent deposit.

It is probable that the adsorption of these salts or their oxidation products as CO_2 or fluoride ions on the anodic oxide films protects them from oxidation. Sodium fluoride and sodium carbonate also assist the buffering of the solution.

The Effect of Ammonium Salts

Ammonium salts prevent the precipitation of manganese ions or other manganese salts as the *p*H is raised by the addition of ammonium hydroxide. Also they improve the buffering capacity and stability of the manganese complex present and increase the conductivity of the electrolyte.

The Effect of Current Density

Increase of current density leads to the formation of an oxide with a high percentage of MnO_2 or Co_2O_3. This is quite distinct in the case of MnO, CoO and Co_3O_4 oxides. Decrease in the current density with Mn_2O_3, Mn_3O_4 and Co_3O_4 oxides promotes the formation of a lower oxide, due to the small rate of the anodic reactions involving formation of higher oxides compared to reducing action of the reducing agents present towards these higher oxides.

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Some Azido and Cyanato Complexes of Bivalent Metals Containing Bipyridyl and o-Phenanthroline

R. C. DAS, M. K. MISHRA, B. K. NANDA and A. K. SAHU

Chemistry Dept, University College of Engg., Burla 768 018 Orissa

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Mixed ligand complexes of formulae [MLX_2].nH_2O, where M=Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L=oo'-bipyridyl and o-phenanthroline and X=N_3^- and NCO^- have been isolated and characterised by analyses, molar conductance, magnetic moment, infra-red and electronic spectral data. The azido complexes of Mn(II), Co(II), Ni(II) and Cu(II) have octahedral geometry with azide bridges through a single nitrogen atom. All other compounds have tetrahedral geometry with terminal nitrogen bonded anionic ligands.

AZIDE and cyanate are peculiar anionic ligands with high electron charge density over the nitrogen atoms, which makes a metal bind to the ligand either terminally through the nitrogen atom or in a bridged manner[1]. We report in this paper our studies on the azido and cyanato complexes of some bivalent metal ions containing two common diamine ligands viz. *oo'*-bipyridyl and *o*-phenanthroline (MLX_2 nH_2O type, where L=diamine and X=anionic ligand).

Materials and Methods

All chemicals used were of pure grade and solvents were used after distillation.

1 m. mole of metal chloride or nitrate was dissolved in ~2 ml. of water and was treated with slight excess of the diamine in ~5 ml. of alcohol. The solution was warmed and to it stoichiometric amount of dilute aqueous solution of sodium azide or potassium cyanate was added. The mixture was refluxed for 30 minutes to ensure completion of reaction. The precipitated complex was filtered and recrystallised from DMSO and vacuum.dried.

Magnetic moments were measured from solid specimens using Gouy method. Molar conductance, UV and visible spectra were measured from DMSO/methanol solutions. Infra-red spectra were recorded in the range 4000-650 cm^{-1} in KBr discs.

Results and Discussion

Table 1 gives the analytical, melting point and magnetic moment data along with characteristic infra-red absorption band positions of the anionic ligands after complexation.

All the compounds are non-electrolytes having very low molar conductance values.

Azido complexes—All the compounds (excepting Cd(II) and Zn(II) complexes) have magnetic moments fairly within the normal range of spin-free octahedral complexes, although the magnetic moments of only Co(II) and Ni(II) complexes are diagonistic of their structures.

The charge-transfer absorptions may be divided into three categories. The first set of bands belonging to intra-ligand $\pi \rightarrow \pi^*$ origin[2-4] occur at 47,620-45,450 cm^{-1} ; 44,250-40,320 cm^{-1} and 37,665-33,220 cm^{-1}. The second category (34,480-32,360 cm^{-1})[2-4] is possibly due to ligand-metal charge-transfer. The third band (26,670-23,470 cm^{-1}) occurs often as a split band and possibly arises out of $e_g \rightarrow \pi^*$, metal-ligand charge-transfer[2-4].

The ligand field bands of Cu(II) complexes appear as a broad band having the centre of gravity at 14,925 cm^{-1} (*oo'*-bipyridyl) and 15,210 cm^{-1} (*o*-phenanthroline), at the same positions and intensities reported by Dutta and De[5]. The positions, intensities and shapes of the absorption bands are diagonistic of a distorted octahedral structure with CuN_6 chromophore[6]. Using Billing and Underhill's procedure[7], the 10 Dq values have been calculated to be 7,462 and 7,610 cm^{-1} for bipyridyl and *o*-phenanthroline complexes respectively.

The only ligand field bands observed in case of nickel(II) complexes are at 17,500 cm^{-1} and 16,810 cm^{-1} respectively, owing to the transition $^3A_{2g} \rightarrow ^3T_{1g}$ (F) (ν_2 transition). The positions and intensities of the bands, associated with the μ_{eff} values (3.28 and 2.90 BM respectively) clearly indicate octahedral symmetry with the complexes[8,9]. The ν_3 band appears to have been obscured by the intense M→L charge transfer bands and the spectra have not been recorded over the range to get the ν_1 band. A band at 15,500 cm^{-1} observed in $Ni(bp.)(N_3)_2$ is perhaps due to a spin-forbidden transition.

Co(II) complexes give clear ligand field bands[8] $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (ν_1) at 7,565 and 7,690 cm^{-1},

TABLE—1

COLOUR, ANALYSES, MAGNETIC MOMENT AND INFRA-RED SPECTRAL DATA OF AZIDO AND CYANATO COMPLEXES

Compounds	Colour[a]	Melting point (°C)	Analyses data[b] %M.	Analyses data[b] %N.	μ_{eff} (B.M.)	Infra-red spectral bands (cm^{-1})[c] ν_s	$\nu_{as.}$	$\nu_s+\nu_{as.}$
$Mn(bp)(N_3)_2$	Light yellow	281	18.4 (18.61)	32.9 (33.28)	5.80	1315 sh	2098 vs 2060 sh	3330 w
$Co(bp)(N_3)_2$	Brick red	288	19.8 (19.70)	32.8 (32.78)	4.70	1315 s	2095 vs 2049 sh	3350 w, br
$Ni(bp)(N_3)_2$	Green	234	19.8 (19.64)	32.8 (32.81)	3.28	1300 m	2090 vs 2050 sh	
$Cu(bp)(N_3)_2$	Yellowish green	224	20.7 (20.55)	32.0 (32.29)	1.84	1315 m	2000 vs, br	
$Cd(bp)(N_3)_2$	White	288	31.8 (31.88)	27.8 (27.81)	—	1285 s	2070 vs	3340 w
$Hg(bp)(N_3)_2$	White	220	45.6 (45.50)	22.1 (22.25)	—	1315 s	2035 vs	
$Mn(o\text{-}phen)(N_3)_2$	Pale yellow	280	17.3 (17.21)	30.5 (30.73)	5.85	1280 m	2090 sh 2050 vs	3250 w, br
$Co(o\text{-}phen)(N_3)_2$	Brick red	>300	18.2 (18.23)	30.1 (30.35)	4.66	1290 m	2060 vs 2035 sh	3220 w, br
$Ni(o\text{-}phen)(N_3)_2$	Green	255	18.2 (18.16)	30.1 (30.37)	2.90	1300 m	2075 vs 2050 sh	3300 w, br
$Cu(o\text{-}phen)(N_3)_2$	Green	269	19.7 (19.40)	29.8 (29.92)	1.87	1287 m	2055 vs 2040 sh	3250 w, br
$Cd(o\text{-}phen)(N_3)_2$	White	213	30.9 (29.84)	26.0 (26.04)	—	1285 m	2050 vs	3300 w, br
$Mn(bp)(NCO)_2.6H_2O$	Light brown	280	13.7 (13.63)	13.7 (13.90)	5.88	—	2180 vbr	
$Ni(bp)(NCO)_2.H_2O$	Green	254	18.5 (18.52)	17.6 (17.68)	3.78	—	2160 sh 2215 s	
$Cu(bp)(NCO)_2$	Blue	186	20.7 (20.55)	18.6 (18.75)	2.10	—	2180 vbr	
$Cd(bp)(NCO)_2$	White	292	31.5 (31.88)	15.8 (15.89)	—		2205 s, br	
$Mn(o\text{-}phen)(NCO)_2.3H_2O$	Pale yellow	275	14.7 (14.70)	14.8 (15.02)	5.40		2160 s 2210 s	
$Co(o\text{-}phen)(NCO)_2$	Deep blue	264	17.9 (18.23)	17.3 (17.34)	4.82		2180 s 2200 sh	
$Ni(o\text{-}phen)(NCO)_2.3H_2O$	Green	261	15.5 (15.57)	14.7 (14.86)	4.16		2180 vs, br	
$Cu(o\text{-}phen)(NCO)_2$	Blue	201	19.3 (19.40)	16.8 (17.10)	2.12		2165 s 2210 s	
$Cd(o\text{-}phen)(NCO)_2$	White	266	30.2 (29.84)	14.7 (14.88)	—		2165 sh 2215 s	

a. All compounds are either crystalline or micro crystalline.

b. The values in parenthesis are theoretical values.

c. The ν_s, ν_{as} and combination bands correspond to azide and cyanato group vibrations.

$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) at 15,870 and 15,380 cm^{-1}, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) at 19,530 and 19,720 cm^{-1} respectively for bipyridyl and *o*-phenanthroline complexes. The ν_2/ν_1 ratio[9] ($\sim$2.05), 10Dq value[9] (8,305 and 7,690 cm^{-1}), $\mu_{eff.}$[8] (4.70 and 4.66 B.M) indicate the complexes to be octahedral.

Mn(II) complexes gave very weak ligand field bands which could not be detected clearly, because of their very low solubility.

The infra-red spectra of the compounds contain modified bands of the amines and azide groups indicating their co-ordination. The $\nu_{as.}$ (N_3^-) and ν_s(N_3^-) bands of azide generally appear at $\sim$2,100 and $\sim$ 1,300 cm^{-1} respectively[10-13]. A very weak band also appears at $\sim$ 3,400 cm^{-1} for a $\nu_{as}+\nu_s$ combination.[13] Nelson et al.[12] and Ziola et al.[14] have shown that in a symmetric bridged structure ν_s is either i.r. inactive or very weak unlike the case of cyanates[12], whereas i.r. active band at $\sim$ 1,300 cm^{-1} is diagonistic of terminal and single atom bridged structures. Since such type of i.r. spectra are observed for Mn(II), Co(II), Ni(II) and Cu(II) complexes and they are all suggested to be octahedral from electronic spectra and magnetic moment data, the azide must obviously be having a single atom bridged type structure. Cd(II) and Hg(II) have difference in the ν_{as}(N_3^-) as single bands unlike the split one in the others. The azide ion may be linked terminally and the compounds may be of tetrahedral type as is generally the case with Cd(II) and Hg(II) complexes.

Cyanato complexes—The magnetic moments of the compounds are well within the range prescribed for tetrahedral complexes.

The charge transfer transitions occur as three distinct bands. In the case of bipyridyl complexes an additional weak shoulder appears at ~ 46,500 cm^{-1} to the band at ~ 40,000 cm^{-1}. In the case of all the *o*-phenanthroline compounds and Cd(bp) $(NCO)_2$ they merge into a single band. As assigned in the corresponding azido complexes, the above bands together with the band at 37,665-33,555 cm^{-1} belong to the intra-ligand π—π^* origin. The second category of bands fall into the region 34,720-32,360 cm^{-1}, possibly due to ligand→metal charge transfer. The third category of bands are not observed; possibly they move to higher energy and get enveloped by the intense higher energy bands.

A single broad band in the ligand field region occur at 13,700 and 14,050 cm^{-1} for bipyridyl and *o*-phenanthroline complexes of Cu(II) respectively, for the $^2T_{2g} \rightarrow {}^2E_{2g}$ transition. The Co(II) complexes show the ligand field bands in two closely spaced groups. The first group correspond to $^4A_2 \rightarrow {}^4T_1(F)$ transition (ν_2, 6,900 and 7,700 cm^{-1}) occurring at the same positions for both the diamine(L) complexes. The second group (ν_3) corresponding to $^4A_2 \rightarrow {}^4T_1(P)$ transition occur at 15,800; 16,420; 17,420 and 15,750; 16,450; 17,390 cm^{-1} for Co(bp) $(NCO)_2$ and Co(*o*-phen) $(NCO)_2$ complexes respectively. The general pattern of bands of Cu(II) and Co(II) complexes correspond to tetrahedral structure[8,9]. Supporting evidence to this may be obtained from the magnetic moment for Cu(II) ($\mu_{eff.}$>2B.M)[8] and Co(II) ($\mu_{eff.}$ 4.4-4.8 B.M.)[8].

Ni(II) exhibits weak bands at 15,380 (ϵ 60); 13,160(ϵ31); 9,610(ϵ 34) and 17,860(ϵ 36); 12,820(ϵ 26); 8,330(ϵ 13) cm^{-1} for both bipyridyl and *o*-phenanthroline complexes respectively. The band positions and intensities are more or less similar to those of octahedral complexes. Since the magnetic moment data, in the solid state, clearly point to tetrahedral structure, it is assumed that Ni(II) complexes probably enter into solvation during solution. There is an observed weakening of colour in solution. However, our attempts to isolate the adduct for complete characterisation failed.

Mn(II) complexes have very weak absorptions in the ligand field region to record. In analogy with other cyanato complexes, they are also assumed to be tetrahedral.

The infra-red spectra, besides containing modified bands of amines contain the vibrations of the cyanato group. Although $\nu_{as.}$ vibration poorly characterise the bonding of the cyanato group, a diagonistic result may be obtained from the ν_s (NCO^-) vibration[12,15-17]. The $\nu_{as.}(NCO^-)$ is observed as a doublet centering around 2,200 cm^{-1}, whereas the region 1,380 – 1,200 cm^{-1} is completely transparent excepting a modified vibration of the hetero ligand. It suggests a terminal N-bonded cyanato group.[12,15-17]

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Studies of Vanadyl Complexes of Phthalic Acid and Substituted Phthalic Acids

N. G. PALASKAR

Department of Chemistry, S. B. E. S. College of Science, Aurangabad—431 001

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The interactions of vanadyl ion with phthalic acid and 3-chloro, 3-bromo, 3-iodo, 3-nitro, 4-nitro and 3 : 6-dichlorophthalic acids have been investigated by Bjerrum-Calvin pH-titration technique as adopted by Irving and Rossotti at 30° and μ = 0.1 *M* $NaClO_4$ in aqueous medium. The linear relation between metal-ligand stability constants and proton-ligand stability constants was critically examined for complexes of vanadyl ion.

VANADYL complexes of acetylacetone[1], 3-hydroxyquinoline[2], N,N'-dihydroxy-EDTA[3], 1,10-phenanthroline[3], tiron(2,4-dihydroxybenzene-1, 3-disulphonic acid[3]), *o*-hydroxyacetophenone oxime[4], etc., have been reported in the literature. The present work deals with a systematic study of stability constants of complexes of some substituted phthalic acids with vanadyl ion in aqueous medium of 0.1 *M* ($NaClO_4$). This is a continuation of the earlier work on uranyl chelates of phthalic acids[5].

Experimental

Chemicals : Phthalic acid, sodium hydroxide, sodium perchlorate and perchloric acid were obtained from E. Meck. 3-nitrophthalic acid, 4-nitrophthalic acid and 3,6-dichlorophthalic acid were procured from British Drug House, India. 3-chlorophthalic acid, 3-bromophthalic acid and 3-iodophthalic acid were prepared by standard method. All solutions were prepared by using double distilled carbon dioxide free water.

Metal salt solution : Vanadyl sulphate of AnalaR (BDH) quality was used and $Vo(OH)_2$ was precipitated by the addition of sodium hydroxide solution. The vanadyl hydroxide was washed free from the sulphate ion and was then dissolved in perchloric acid to obtain a stable vanadyl perchlorate solution.

pH-meter : Beckman model H-2 *p*H-meter, in conjunction with Beckman standard general purpose glass electrode and a saturated calomel electrode, was used for the potentiometric titrations. The measurements could be made with an accuracy of ±0.02 *p*H unit and the reproducibility of the readings was of the same order. The *p*H-meter was calibrated using Cambridge buffer tablets of *p*H 4.01 and 9.11. The temperature of the solutions in the titration vessel was maintained at 30° with a thermostatic arrangement.

Calvin-Bjerrum titration : The experimental procedure involved potentiometric titration of solutions of (i) free $HClO_4$, (ii) free $HClO_4$ + reagent, (iii) free $HClO_4$ + reagent + vanadyl ion and (iv) free $HClO_4$ + vanadyl ion against standard NaOH solution added from microburette giving an accuracy of 0.025 ml. The ionic strength of the solution for each set was maintained at 0.1 *M* by the addition of appropriate quantity of $NaClO_4$ solution. The titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through an assembly containing the electrodes, to keep away CO_2.

Results and Discussion :

Irving and Rossotti expression[6] was used for the calculations of $\bar{n}$ values[6] which were used for the determination of stability constants of vanadyl complexes. Factors like hydrolysis of vanadyl ion, presence of polynuclear hydrogen and hydroxyl ions was assumed absent. The assumptions were justified on the following grounds :

(i) The departure of the metal complex titration curve from the reagent curve commences from about *p*H 2.4 which is less than the *p*H of hydrolysis of metal ion. The variation of $\bar{n}$ is continuous up to 1 after which there occurs an abrupt change showing thereby the formation of 1 : 1 complex and absence of 1 : 2 complex.

(ii) The solution employed being very dilute, the probability of existence of polynuclear species under experimental conditions is not expected to be high.

Approximate values of log K_1 were obtained by half-integral method. The accurate values obtained by pointwise calculations are reported in Table 1.

TABLE 1

STABILITY CONSTANTS

Temp. : 30°C $\mu = 0.1$ M ($NaClO_4$)

Sl. No.	Name of the ligand	pK_1^*	pK_2^*	log K_1
1.	Phthalic acid	2.80	5.00	3.94
2.	3-chlorophthalic acid	2.28	4.89	3.91
3.	3-bromophthalic acid	2.43	4.29	3.77
4.	3-iodophthalic acid	2.48	4.62	3.49
5.	3-nitrophthalic acid	1.80	3.93	3.08
6.	4-nitrophthalic acid	1.98	3.98	2.93
7.	3 : 6-dichlorophthalic acid	1.40	3.40	2.99

* Ref. 7.

Complexation reaction :

In all cases the pH value when $\bar{n}=1$ is about 4. The pK_1 values of all ligands are less than 4, which indicates the dissociation of one carboxylate group before the complexation. In general, therefore, the complexation reaction can be represented as :

$$VO^{2+} + HL^- = VoL + H^+$$

Validity of log K = a pK + b relation :

The values of log K_1 are plotted against pK_2 values[7] in Fig.1. It can be seen from this plot that

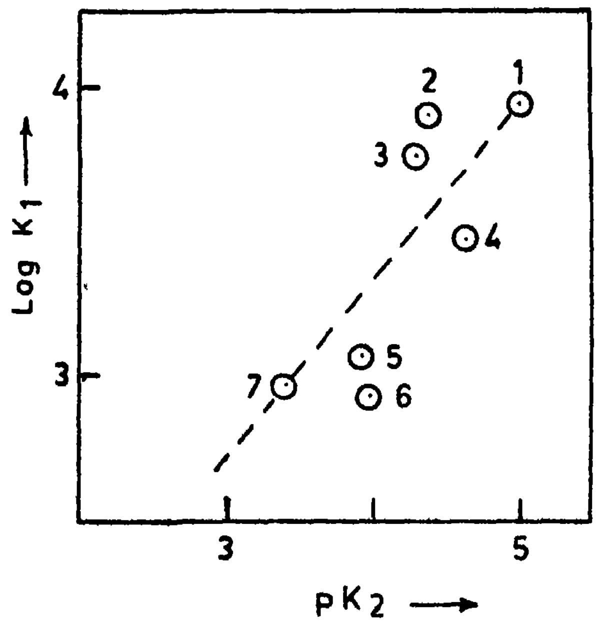


Fig. 1. Plot of log K_1 *vs* pK_2. Ligand numbers as given in Table 1.

a single straight line passing through all the points cannot be drawn. However, two straight lines one for points corresponding to the vanadyl complexes of phthalic acid, 3-iodophthalic acid, 3-nitrophthalic acid and 4-nitrophthalic and another for 3-chlorophthalic acid, 3-bromophthalic acid and 3 : 6-dichlorophthalic acid can be drawn.

If the changes in the partial molar free energies of the metal-ligand and proton-ligand complexes exactly compensated each other, log K_1 *vs* pK_2 plot should give a straight line with unit slope. When such a line passing through the phthalic acid complex was drawn, shown by dotted line, the point corresponding to the complex of 3 : 6-dichlorophthalic acid alone fell on the line whereas all the remaining points were either above or below the line. The points corresponding to the chelates of 3-iodophthalic acid, 3-nitrophthalic acid and 4-nitrophthalic acid were below and the remaining points were above the line.

The lower stability observed for the chelates of 3-iodophthalic acid and 3-nitrophthalic acid in comparison to their proton-ligand complex may be due to steric factors. The chelate of 4-nitrophthalic acid, however, should not exhibit steric hindrance. The lower stability of this complex can, therefore, be explained on the basis of $d\pi$-$p\pi$ interaction. If π-donation from the oxygen of the carboxylate group to the vanadium is responsible for the chelation, then the nitro group being a π-acceptor, should reduce the π-donation in the 4-nitro chelate though the effect would be too small at the oxygen donor. The "extra stabilization" observed from log K_1 *vs* pK_2 relation for 3-chloro and 3-bromo chelates can be attributed to the fact that the lowering in stability due to the steric hindrance has been more than compensated by π-donation due to these groups.

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Kinetic Studies of the Reaction Between Bromine and Malic Acid (Influence of Hydrogen Ion Concentration)

B. S. RATHOR and K. C. GROVER

Department of Chemistry, University of Jodhpur, Jodhpur.

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The kinetics of the oxidation of malic acid with bromine has been studied. The reaction was found to be of first order with respect to both bromine malic acid—the total order being two. The energy of activation, free energy and entropy of activation were found to be 14.0 K. cal./mole., 15.1 K. cal./mole. and − 3.6 e. u. at pH∼8.75. The reaction rate increases, at first, with rise of pH, reaches a maximum at pH∼9.40 and, then, decreases. The dependence of the rate on pH showed that HOBr is a faster oxidising agent than molecular bromine. The reactive species was found to be a combination of hypobromous acid and bromine molecule with $k_{HOBr} \gg k_{Br_2}$. The oxidation reaction can be represented by the attack of the oxidant on carboxylate ion.

A survey of literature revealed that malic acid has been estimated by different oxidising agents[1-2], but no attempt seems to have been made to oxidise malic acid stoichiometrically to carbon dioxide and water by bromine and to study its reaction mechanism.

Experimental

Materials :

All the chemicals used were B. D. H. 'AnalaR' products and were used without any further purification.

Stoichiometry of the reaction :

The data given in Table 1 show that the reaction between malic acid and bromine is quantitative and that the oxidation takes place to the stage of carbon dioxide and water. The production of carbon dioxide in the end products was tested quantitatively.

Procedure for Kinetic studies :

The procedure given in an earlier communication[3] was followed in this case.

Results and Discussions :

The reaction has been shown to be of first order with respect to each of the reactants (Table 2)—the total order being two. The results in (Table 1) indicate the stoichiometry of the reaction and those in Table 3 show that the reaction is fastest at pH∼9.40. The rate constant decreases with the increase of bromide ion concentration (Table 5) which shows that the reaction with hypobromous acid is faster than that with molecular bromine. The energy of activation, free energy and entropy of activation were 14.0 K. cals./mole, 15.1 K. cals./mole. and − 3.6 e.u. at pH∼8.75 (Table 4).

Experimentally, it has been shown that no complex formation is involved in the system as shown by the plot of 1/k, against 1/sodium malate

TABLE 1

Time = 6 hours Temp. = 35° ± 0.05° pH∼3

Sl. No.	Malic acid taken (ml.)	"Br_2" (0.025 M) added (ml.)	"Br_2" (0.025 M) consumed (ml.)	Malic acid present (gm.)	Malic acid found (gm.)	% Recovery	% Error ±
1.	5.00	5.00	3.60	0.00279	0.00202	Incomplete	—
2.	5.00	10.00	5.01	0.00279	0.00281	100.72	+0.72
3.	6.00	15.00	6.00	0.00335	0.00336	100.30	+0.30
4.	5.00	15.00	5.02	0.00279	0.00281	100.72	+0.72
5.	8.00	25.00	8.02	0.00447	0.00449	100.45	+0.45
6.	8.00	30.00	8.01	0.00447	2.00449	100.45	+0.45
7.	5.00	20.00	5.02	0.00279	0.00281	100.72	+0.72
8.	6.00	25.00	6.02	0.00335	0.00337	100.60	+0.60

TABLE 2

FIRST ORDER CONSTANT WITH RESPECT TO HYPOBROMITE

Temp. = 35 ± 0.05°

Hypobromite = 0.95 × 10^{-3} *M* Sodium thiosulphate = 0.001 *N*

Sodium Malate × 10^{-3}	20.00	16.66	12.50	11.11
$k_1 \times 10^{-3}$ min^{-1}	47.20	39.10	29.40	26.10
k_1/sodium malate	2.3600	2.3469	2.3526	2.3492

Mean value of k_1/sodium malate = 2.3522 ± 0.0078 mole^{-1} min.$^{-1}$

FIRST ORDER CONSTANT WITH RESPECT TO MALIC ACID

Temp. = 35 ± 0.05°

Hypobromite = 11.80 × 10^{-3} *M* Sodium thiosulphate = 0.01 *N*

Sodium malate = 0.188 × 10^{-3} *M* Mean *p*H = 8.10

k_1 = 0.42 × 10^{-3} *M* min^{-1}.

TABLE 3

SECOND ORDER CONSTANTS

Temp. = 35 ± 0.05°

Hypobromite = 5.60 – 6.07 × 10^{-3} *M*

Malic acid = 0.933 – 1.013 × 10^{-3} *M*

Mean *p*H	k litre mole^{-1} sec.$^{-1}$ × 10^{-4}	
3.15	0.13	
4.75	5.13	
6.00	12.00	
6.70	16.67	
7.45	17.38	
8.75	18.00	
8.85	24.00	(0.025 *M* sulphate)
8.85	16.00	(0.025 *M* chloride)
9.40	20.00	
9.80	19.33	
10.65	6.00	
12.10	2.66	

TABLE 4

SECOND ORDER CONSTANTS AT DIFFERENT TEMPERATURES

Bromine = 6.25 × 10^{-3} *M* Malic acid = 0.917 – 1.008 × 10^{-3} *M*

Hypobromite = 5.50 – 6.05 × 10^{-3} *M* Mean *p*H = 8.78

Temp. °C	k litre mole^{-1} sec.$^{-1}$ × 10^{-4}
35	18.00
40	26.00
45	30.00

TABLE 5

EFFECT OF ADDED BROMIDE

Temp. = 35 ± 0.05°

Bromine = 6.25 × 10^{-3} *M* Malic acid = 1.033 × 10^{-3} *M*

Hypobromite = 6.20 × 10^{-3} *M* Mean *p*H = 6.50

Br^- Concentration	k litre mole^{-1} sec.$^{-1}$ × 10^{-4}
Nil	12.00
0.20 *M*	8.66
0.25 *M*	6.00
0.33 *M*	4.00

when a straight line passing through the origin was obtained (Table 2, Fig. 1). The absence of a free radical is indicated by the negative test with mercuric chloride. The fact that the reaction is fast in the

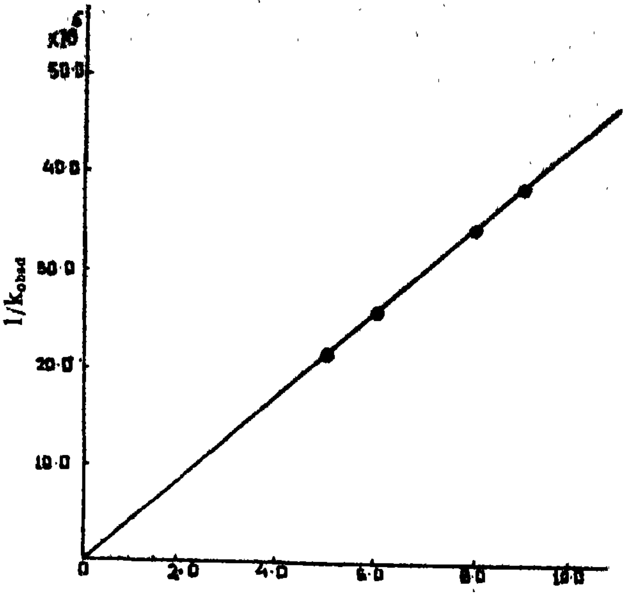


Fig. 1. Sodium malate *vs* Bromine

alkaline medium (*p*H ~ 9.40) agrees quantitatively with the assumption that the anion of the substrate is oxidised much more rapidly than the undissociated molecule.

Reactive species :

On the basis of arguments advanced in the earlier communication, two possibilities[4] could be considered viz., (i) $k_{HOBr} \gg k_{Br_2}$ and (ii) $k_{HOBr} \ll k_{Br_2}$. The value of K_1 ($K_1 = 32.3 \times 10^{-9}$) obtained on the basis of assumption I is nearer to the accepted value[5] (indicated by a cross on the x axis (Fig. 2),

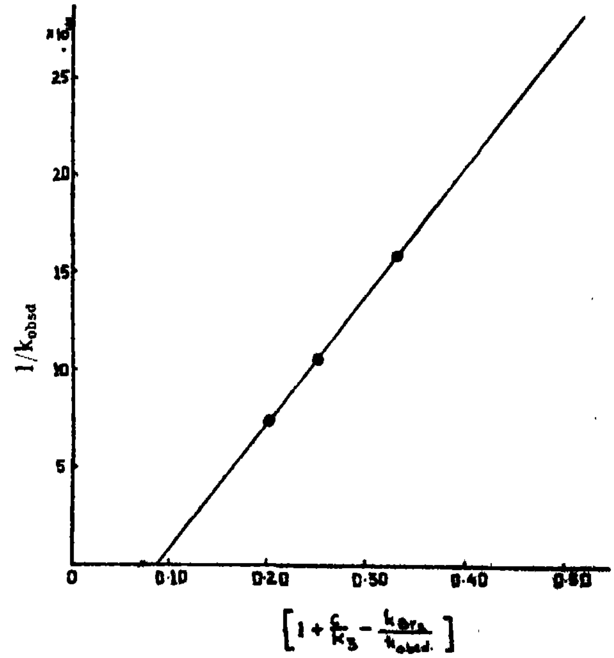


Fig. 2. Malic acid *vs* Bromine

but the value of K_1 ($K_1 = 119.70 \times 10^{-9}$) obtained on the basis of II assumption differs fron the theoretical value. The statement that $k_{HOBr} >> k_{Br_2}$ is supported by these results. The reactive species, therefore, is a combination of hypobromous acid and molecular bromine with $k_{HOBr} >> k_{Br_2}$. This is supported by the results with bromine free hypobromous acid which was prepared by the method of Y. Knoller and B. Perlmutter-Hayman[6]. The value of k with unbuffered and buffered hypobromous acid was found to be 6.66 and 6.00 respectively.

Besides, a plot of rate constant based on Table 3, Fig. 3, against the calculated concentrations of $[HBrO] \times [C_4H_4O_5^-]$ at the middle stage of the

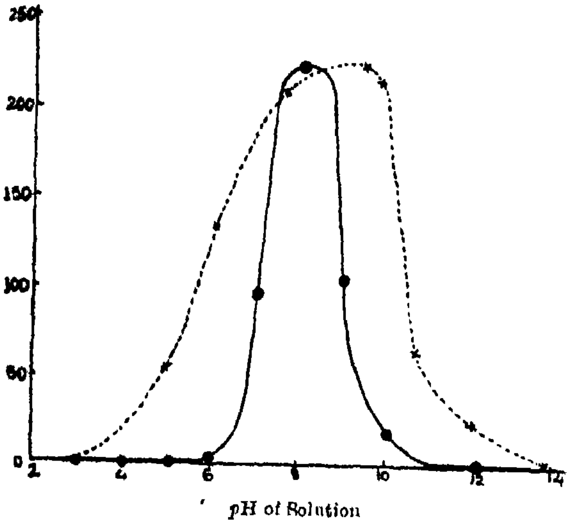


Fig 3. Malic acid vs Bromine

—●— Calculated values of concentrations at the middle stage $[HBrO] \times [H_4C_4O_5] \times 10^8$

···×··· Experimental values of rate constant × 1.1 × 10^4

reaction showed a close parallelism. The slowing down of the reaction beyond pH ~ 9.40 is due to the decrease in the concentrations of HOBr and Br_2, Br_3 does not take part in the oxidation reaction.

TABLE 6

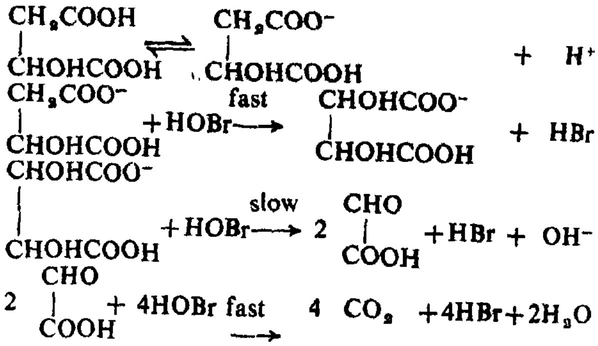
Experimental value of rate constant at 35°		Calculated values of concentrations at middle stage of 35°		
pH	k $\times 10^{-3}$	pH	$[HBrO + Br_2] \times [H_4C_4O_5]^-$ $\times 10^8$	$[HBrO] \times [H_4C_4O_5]^-$ $\times 10^8$
3.15	0.18	2	3.47	2.79×10^{-5}
4.75	5.13	3	29.70	23.83×10^{-4}
6.00	12.00	4	120.30	96.51×10^{-3}
6.70	16.67	5	174.12	13.89×10^{-1}
7.45	17.88	6	187.04	13.90
8.75	18.00	7	221.89	98.95
9.40	20.00	8	248.97	220.98
9.80	19.33	9	103.99	102.99
10.05	6.00	10	19.39	14.89
12.10	2.66	11	1.60	1.56
—	—	12	0.160	0.15
—	—	13	0.016	0.015

Rate constants :

Graphs were plotted for all results and the specific rate constant K_1 (Table 2) and K_2 (Table 3) obtained from the slope of log (a-x) and 1/(a-x) respectively against time in seconds. The hypobromite content of the solution was determined by arsenite method[7] and used for calculation of the rate constants.

Reaction mechanism :

Here, the assumption that, both, hypobromous acid and molecular bromine act as oxidising agents with $k_{HOBr} >> k_{Br_2}$ holds good. Hypobromous acid oxidises malic acid to tartaric acid which is oxidised to carbon dioxide and water through the intermediary of glyoxylic acid as shown below :—



Separate experiments on the oxidation of tartarate ion by bromine showed that the reaction is comparatively slower while the oxidation of glyoxylic acid by bromine is a fast reaction.

Similarly, equations can be written with Br_2 as the other reactive species. However, it has been shown that glyoxylic acid is oxidised much more rapidly by hypobromous acid than by molecular bromine.

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Activity Coefficients for Mixtures of Methylene Chloride with Benzene, Toluene, *o*-, *m*-, and *p*-Xylenes

R. PRATAP SINGH and S. SHRAN SINGH*

Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur

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Activity coefficients for binary liquid mixtures with a common component (1) as methylene chloride and a varying component (2) as benzene, toluene, *o*-, *m*- and *p*-xylenes were calculated from free energy of mixing data and the values were fitted in two constant Margules equation. The infinite dilution activity coefficient values of the components were finally correlated with the carbon numbers of the varying component and the applicability of the correlations was discussed in terms of the existence of mobile liquid structures in these systems.

USUALLY the values of the component activity coefficients are greater than unity and indicate positive deviations from Raoult's law. However, a few classes of liquid mixtures do show values less than unity corresponding to the negative deviations[1] which are the result of weak specific interactions in such systems and much remains to be understood as yet about the systematics of the non-ideality. It was, therefore, considered desirable to calculate the activity coefficients for binary mixtures of methylene chloride with benzene, toluene, *o*-, *m*-, and *p*-xylenes which are known to possess weak specific interactions[2,3] and to correlate the infinite dilution activity coefficients with structural parameters of the pure components.

Results and Discussion

Free energy of mixing G^E of a binary mixture with components 1 and 2 is related with corresponding component activity coefficients γ_1 and γ_2 respectively at temperature T and pressure P, by the equations[4]

$$RT \ln \gamma_1 = G^E + X_2 \left(\frac{\delta G^E}{\delta X_1}\right)_{T,\,P} \quad (1)$$

and
$$RT \ln \gamma_2 = G^E - X_1 \left(\frac{\delta G^E}{\delta X_1}\right)_{T,\,P} \quad (2)$$

where X_1 and X_2 are the component mole fractions. In order to calculate the component activity coefficients from equations (1) and (2), the values of G^E for various compositions of the binary mixtures with component 1 as methylene chloride and component 2 as benzene, toluene, *o*-, *m*-, and *p*-xylenes were taken from the works of Nigam and Mahl[2]. The values of $\left(\frac{\delta G^E}{\delta X_1}\right)_{T,\,P}$ were obtained from G^E versus X_1 plots for suitable mole fractions covering the extreme dilute regions and the corresponding values of $\ln \gamma_1$ and $\ln \gamma_2$ were computed and plotted against X_1 in each case (Fig. 1-A to 1-E).

It may be observed from Fig. 1-A to 1-E that for each binary mixture considered, the curves for $\ln \gamma_1$ and $\ln \gamma_2$ as functions of X_1 are of opposite slope and the gradients $\left(\frac{\delta \ln \gamma_1}{\delta X_1}\right)_{T,\,P}$ and $\left(\frac{\delta \ln \gamma_2}{\delta X_2}\right)_{T,\,P}$ are finite as X_1 and X_2 tend to zero respectively. Also, these curves approach to origin tangentially to the composition axis, i. e., $\left(\frac{\delta \ln \gamma_1}{\delta X_1}\right)_{T,\,P} \to 0$ as $X_1 \to 1$ and $\left(\frac{\delta \ln \gamma_2}{\delta X_2}\right)_{T,\,P} \to 0$ as $X_2 \to 1$.

Further, the values of

$$\left(\frac{\delta \ln \gamma_1}{\delta X_1}\right)_{T,\,P} \text{ and } \left(\frac{\delta \ln \gamma_2}{\delta X_2}\right)_{T,\,P}$$

were found to be consistent with the equation

$$X_1 \left(\frac{\delta \ln \gamma_1}{\delta X_1}\right)_{T,P} - X_2 \left(\frac{\delta \ln \gamma_2}{\delta X_2}\right)_{T,\,P} = 0 \quad (3)$$

within the limits of experimental error. These tests provide a check for the isothermal phase data of Nigam and Mahl[2].

In order to fit the activity coefficient data in two constant Margules equation

$$\ln \gamma_1 = (2A_{21} - A_{12})X_2^2 + 2(A_{12} - A_{21})X_2^3 \quad (4)$$

and

$$\ln \gamma_2 = (2A_{12} - A_{21})X_1^2 + 2(A_{21} - A_{12})X_1^3 \quad (5)$$

$\ln \gamma_1/X_2^2$ and $\ln \gamma_2/X_1^2$ were plotted as functions of X_2 and X_1 respectively in each case. The plots for a typical system are given in Fig. 2-A and 2-B.

* Department of Chemistry, Bhagalpur University, Bhagalpur—812 007

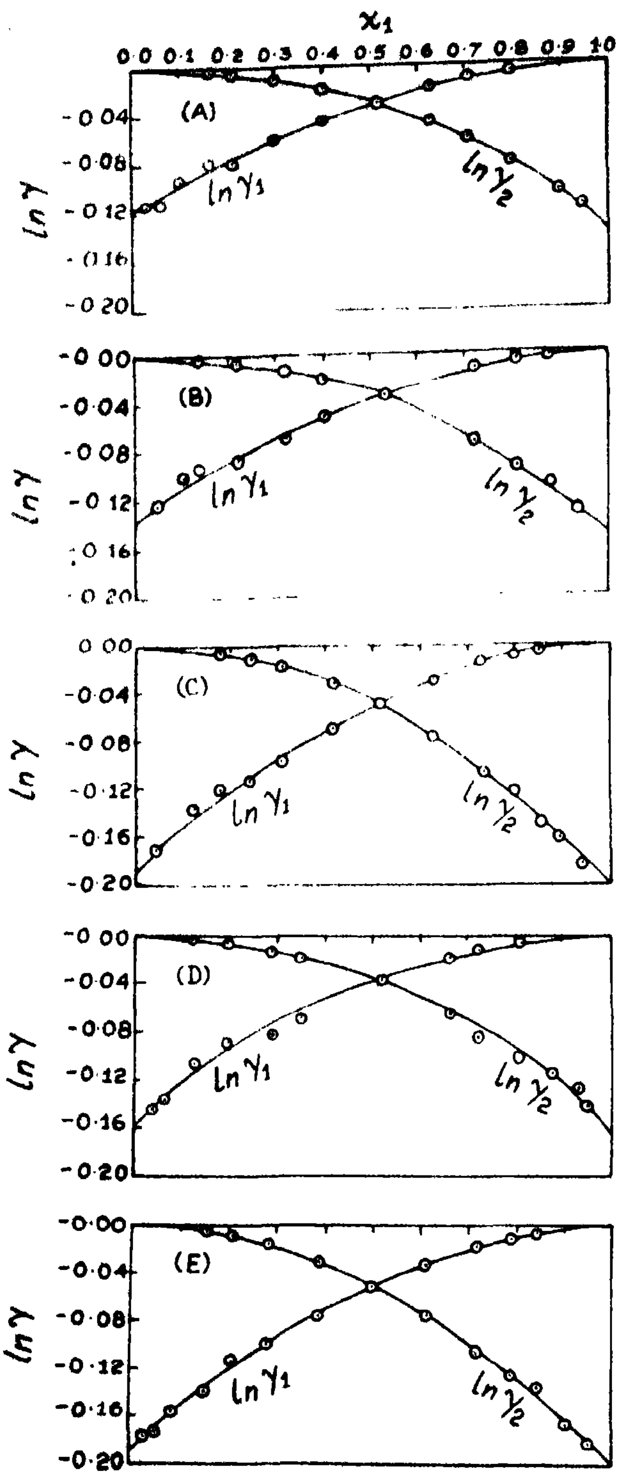


Fig. 1. Plots of ln γ vs X_1 for binary mixtures of
(A) $CH_2Cl_2+C_6H_6$,
(B) $CH_2Cl_2+C_6H_5CH_3$,
(C) $CH_2Cl_2+o\text{-}C_6H_4(CH_3)_2$,
(D) $CH_2Cl_2+m\text{-}C_6H_4(CH_3)_2$
and (E) $CH_2Cl_2+p\text{-}C_6H_4(CH_3)_2$

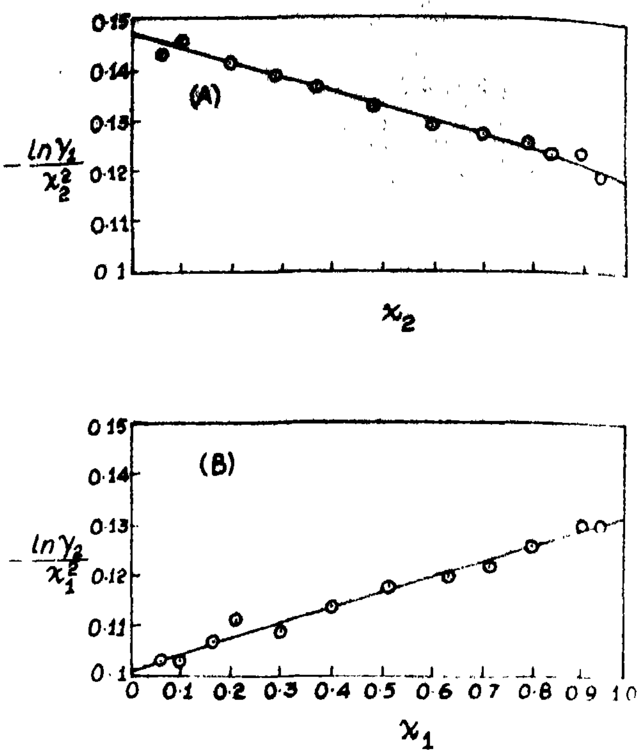


Fig. 2. Plots of (A) $\ln \gamma_1/x_2^2$ vs. X_2 and (B) $\ln \gamma_2/x_1^2$ vs. X_1 for mixtures of methylene chloride with benzene

As expected all these plots were straight lines and as such the constants A_{12} and A_{21} were calculated from the corresponding slopes and intercepts in each case. Further, for infinite dilution conditions equations (4) and (5) give

$$\ln \gamma_1^0 = A_{12} \qquad (6)$$

and

$$\ln \gamma_2^0 = A_{21} \qquad (7)$$

where $\ln \gamma_1^0$ and $\ln \gamma_2^0$ are the infinite dilution activity coefficients of components 1 and 2 respectively. The values of constants A_{12} and A_{21} as obtained from the curves similar to Fig. 2-A and 2-B for each system are compared with the corresponding values of $\ln \gamma_1^0$ and $\ln \gamma_2^0$ obtained from Fig. 1-A to 1-E in Table 1.

For the systems included in Table 1, the component 1 is fixed and the component 2 is varied by the substitution of $-CH_3$ group in benzene ring. If we consider the infinite dilution condition with $X_1 \to O$ for such systems, the entire component 1 forms the solute species and the component 2 forms the solvent environment or the bulk. In such situation $\ln \gamma_1^0$ values may be correlated according to Black et al[5] by the following equation

$$\ln \gamma_1^0 = K + (B/n_2)n_1 + F/n_2 \qquad (8)$$

where n_1 and n_2 are the carbon numbers of the components 1 and 2 respectively; while K, B and

TABLE 1

VALUES OF A_{12}, A_{21}, $\ln \gamma_1^0$ AND $\ln \gamma_2^0$ FOR BINARY MIXTURES OF METHYLENE CHLORIDE WITH BENZENE, TOLUENE, o-, m-, AND p-XYLENES

Temp. = 30°

Sl. No.	System	A_{12}: $\ln \gamma_1/X_2^2$ vs. X_2 plot	A_{12}: $\ln \gamma_2/X_1^2$ vs. X_1 plot	A_{12}: Average	$\ln \gamma_1^0$	A_{21}: $\ln \gamma_1/X_2^2$ vs. X_2 plot	A_{21}: $\ln \gamma_2/X_1^2$ vs. X_1 plot	A_{21}: Average	$\ln \gamma_2^0$
1.	$CH_2Cl_2+C_6H_6$	−0.119	−0.115	−0.1170	−0.117	−0.133	−0.132	−0.1325	−0.129
2.	$CH_2Cl_2+C_6H_5CH_3$	−0.140	−0.139	−0.1395	−0.142	−0.155	−0.149	−0.1520	−0.152
3.	$CH_2Cl_2+o\text{-}C_6H_4(CH_3)_2$	−0.185	−0.191	−0.1880	−0.190	−0.201	−0.205	−0.2030	−0.200
4.	$CH_2Cl_2+m\text{-}C_6H_4(CH_3)_2$	−0.160	−0.155	−0.1575	−0.162	−0.167	−0.160	−0.1635	−0.168
5.	$CH_2Cl_2+p\text{-}C_6H_4(CH_3)_2$	−0.195	−0.190	−0.1925	−0.190	−0.206	−0.200	−0.2030	−0.200

F are homologous correlation constants. As the component 1 remains unchanged in each case, n_1 is constant and the above equation can be written as

$$\ln \gamma_1^0 = K + K'/n_2 \quad \ldots \quad (9)$$

where K' is equal to $(B\,n_1+F)$. The constant K is a function of both the components 1 and 2, B is characteristic of the bulk which is formed by the varying component 2 when $X_1 \rightarrow O$ and F is characteristic of its functional group.

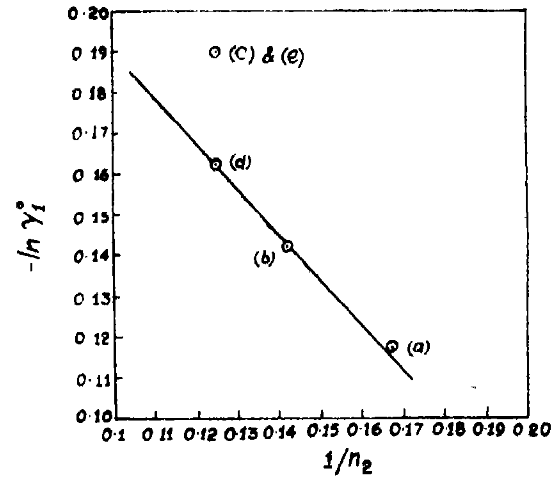


Fig. 3. Plot of $\ln \gamma_1^0$ *vs.* $1/n_2$ for binary mixtures of CH_2Cl_2 with (*a*) C_6H_6, (*b*) $C_6H_5CH_3$, (*c*) $o\text{-}C_6H_4(CH_3)_2$, (*d*) $m\text{-}C_6H_4(CH_3)_2$ and (*e*) $p\text{-}C_6H_4(CH_3)_2$

As required by equation (9), the plot of $\ln \gamma_1^0$ versus $1/n_2$ (Fig. 3) should be a straight line. It is obvious from Fig. 3 that the systems $[CH_2Cl_2+C_6H_6)$, $(CH_2Cl_2+C_6H_5CH_3)$ and $[CH_2Cl_2+m\text{-}C_6H_4(CH_3)_2]$ fall on a straight line; while the systems $[CH_2Cl_2+o\text{-}C_6H_4(CH_3)_2]$ and $[CH_2Cl_2+p\text{-}C_6H_4(CH_3)_2]$ show $\ln \gamma_1^0$ values higher than expected. If these are to fall on the same straight line, $o\text{-}C_6H_4(CH_3)_2$ and $p\text{-}C_6H_4(CH_3)_2$ both are to be assigned an effective carbon number equal to 10. Higher effective carbon numbers for $o\text{-}C_6H_4(CH_3)_2$ and $p\text{-}C_6H_4(CH_3)_2$ in comparison to $m\text{-}C_6H_4(CH_3)_2$ simply indicate that their solutions with CH_2Cl_2 are more non-ideal than that of $m\text{-}C_6H_4(CH_3)_2$ with CH_2Cl_2. This is expected because of the *o*-, *p*-, directing methyl group as substituent in the benzene ring which makes the second methyl group in these positions to contribute more towards non-ideality in comparison to the case where the second methyl group is in the *m*-position. It may be pointed out in this connection that effective carbon numbers have been assigned to take care of structural effects in other cases[8] also.

On the other hand, if we consider these systems at the other extreme of infinite dilution with $X_1 \rightarrow 1$, the common component 1 forms the solvent environment or bulk and the entire component 2 forms the solute species. For such situations where the solvent environment is constant and solute species vary homologously, the following analytical expression is given by Black et al[8]

$$\ln \gamma_2^0 = K + B\,n_2 + C/n_2 \quad \ldots \quad (10)$$

where K again depends on component 1 and 2 both, B is characteristic of the solvent environment

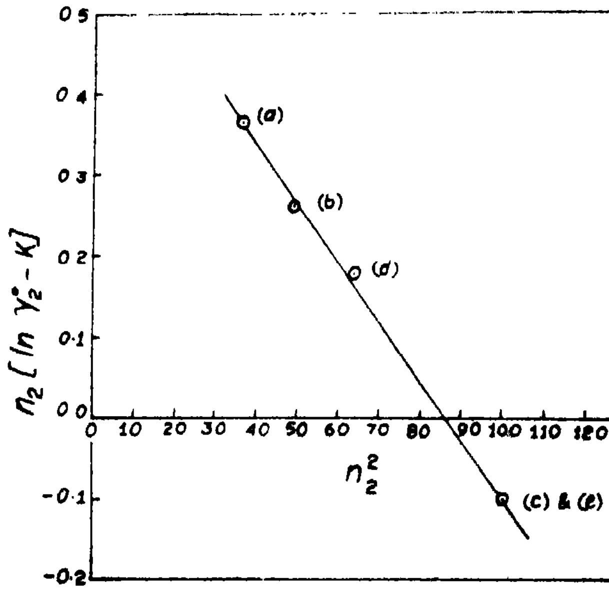


Fig. 4. Plot of n_2 ($\ln \gamma_2^0 - K$) versus n_2^2 for binary mixtures of CH_2Cl_2 with
(a) C_6H_6, (b) $C_6H_5CH_3$, (c) $o\text{-}C_6H_4(CH_3)_2$, (d) $m\text{-}C_6H_4(CH_3)_2$ and (e) $p\text{-}C_6H_4(CH_3)_2$

and C is characteristic of the functional group in varying component 2. Equation (10) for the systems considered here can be rearranged in the following form

$$n_2 [\ln \gamma_2^0 - K] = B\, n_2^2 + C \qquad (11)$$

In order to test the validity of equation (11), as well as that of the assignment of effective carbon number for o-$C_6H_4(CH_3)_2$ and p-$C_6H_4(CH_3)_2$, in the systems under consideration, the value of K as determined from the intercept of the line in Fig. 3 was substituted in equation (11) and $n_2[\ln \gamma_2^0 - K]$ was plotted against n_2^2 in Fig. 4 which gave a fair straight line as required.

In this connection it may be pointed out that Black et al[8] consider the component which tends to zero as the solute species. But this may not always be true in those systems where mobile liquid structures with one component of the binary mixture as the central and the other as the surrounding molecules are formed due to weak specific interactions as concluded from the mixture viscosity data[8]. Nevertheless, the fair applicability of equations (9) and (11) may be explained in the light of an earlier publication by the authors[6]. Their findings relevent for the purpose here are being given in Table 2.

It may be seen from Table 2 that for the infinite dilution situation with $X_1 \to O$ the components providing central as well as surrounding molecules in the mobile liquid structures and the component providing the bulk molecules for the binary mixtures considered are represented by columns III, IV and V respectively. A close scrutiny of column V reveals that the varying component 2 forms the bulk, while the common component 1 entirely remains in the form of mobile liquid structures. Though the liquid structures in each case are not similarly constituted, as is apparent from columns III and IV, yet the deviation in any response due to constitutional non-similarity in these mobile liquid structures becomes insignificant in comparison to the deviations produced by the extent of structuration due to the varying nature of the component forming the bulk or solvent environment. This is so because the concentration of the liquid structures tends to zero as $X_1 \to O$. As such equation (9) correlates satisfactorily $\ln \gamma_2^0$ values with carbon numbers of the varying component alone which forms the bulk and any deviation from the requirements of equation (9) may thus justifiably be corrected by assigning an effective carbon number to only component 2 of a deviating system.

On the other hand, for the infinite dilution situation with $X_1 \to 1$, the components providing the central and surrounding molecules in the solute species in the form of mobile liquid structures and the component providing the bulk or solvent environment are represented by columns VI, VII and VIII respectively. It is clear from column VIII that the common component 1 forms the bulk in each case. Obviously, the entire amount of the varying component 2 forms the solute species or the mobile liquid structures. In this case again as $X_1 \to 1$, the concentration of the liquid structures tends to zero and as such the deviation in any response due to constitutional non-similarity of the liquid structures becomes insignificant in comparison to the deviation produced by the extent of structuration caused by the varying nature of component 2. This explains the applicability of equation (11) for correlation of $\ln \gamma_2^0$ with the carbon numbers of the varying component 2 in each case.

From the above, it is apparent that for the binary mixtures with one component common and the other varying homologously, the infinite dilution activity coefficients can satisfactorily be correlated with the carbon numbers of the varying component. However, in special cases, effective carbon numbers may be assigned to take care of special structural features and the structural non-similarity in the mobile liquid structures existing in the infinitely dilute binary mixtures produce insignificant deviation in comparison to that due to the extent of structuration caused by homologous structural variations in the varying component.

TABLE 2

CONSTITUENT COMPONENTS OF LIQUID STRUCTURES AND THE BULK IN BINARY LIQUID MIXTURES OF METHYLENE CHLORIDE WITH BENZENE, TOLUENE, o-, m- AND p-XYLENES

Sl. No.	System	Liquid Structures for $0<X_1<0.5$			Liquid Structures for $0.5<X_1<1.0$		
		Component providing central molecule	Component providing surrounding molecule	Component providing bulk molecule	Component providing central molecule	Component providing surrounding molecule	Component providing bulk molecule
(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
1.	$CH_2Cl_2 + C_6H_6$	C_6H_6	CH_2Cl_2	C_6H_6	C_6H_6	CH_2Cl_2	CH_2Cl_2
2.	$CH_2Cl_2 + C_6H_5CH_3$	CH_2Cl_2	$C_6H_5CH_3$	$C_6H_5CH_3$	$C_6H_5CH_3$	CH_2Cl_2	CH_2Cl_2
3.	$CH_2Cl_2 + o$-$C_6H_4(CH_3)_2$	o-$C_6H_4(CH_3)_2$	CH_2Cl_2	o-$C_6H_4(CH_3)_2$	o-$C_6H_4(CH_3)_2$	CH_2Cl_2	CH_2Cl_2
4.	$CH_2Cl_2 + m$-$C_6H_4(CH_3)_2$	CH_2Cl_2	m-$C_6H_4(CH_3)_2$	m-$C_6H_4(CH_3)_2$	CH_2Cl_2	m-$C_6H_4(CH_3)$	CH_2Cl_2
5.	$CH_2Cl_2 + p$-$C_6H_4(CH_3)_2$	CH_2Cl_2	p-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$	p-$C_6H_4(CH_3)_2$	CH_2Cl_2	CH_2Cl_2

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Oxidation Kinetics of Diethanolamine by Chloramine-T

MUNESH CHANDRA, SANKAR LAL and O. P. BANSAL

Chemical Laboratories, Agra College, Agra

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Kinetics of chloramine-T oxidation of diethanolamine in alkaline media has been investigated. The reaction is first-order both in amine and oxidant. The order in alkali is found to be nearly −1. The effect of varying the ionic strength on the rate of oxidation is negligible. It is proposed that the amine reacts in a slow step with p-toluenesulphochloramide to form an intermediate compound which subsequently interacts with another molecule of p-toluenesulphochloramide in a faster step yielding formaldehyde and other final products.

EXCEPTING the oxidation kinetics of diethanolamine by potassium persulphate[1] and potassium hexacyanoferrate(III)[2], little is known about the kinetics and mechanism of the oxidation of this substrate by other oxidants. The present paper reports the results of our kinetic investigations on the oxidation of diethanolamine in alkaline media. The main object has been to elucidate the reaction and mechanism and put forward a rate law consistent with the experimental data.

Experimental :

E. Merck (*Pro analysi*) sample of chloramine-T was used and the solution was stored in black coated bottle to prevent photo-chemical decomposition. The strength was determined using iodometric method[3]. All other chemicals used were either A.R. R. or extra pure quality and their solutions were prepared using doubly distilled water in pyrex vessels. The reaction vessels were coated with black varnish to exclude photo-chemical effects.

The requisite amounts of chloramine-T and sodium hydroxide solutions of desired concentrations were placed in a reaction vessel. This mixture and the amine solution of desired concentration were kept separately in a thermostated bath maintained at the desired temperature (±0.1°). The reaction was started by adding the requisite volume of the amine solution to the mixture. The progress of the reaction was followed by estimating the unconsumed chloramine-T iodometrically. Owing to the high initial concentration of the alkali, the *p*H remained constant during the reaction.

Results :

To determine the number of moles of chloramine-T consumed per mole of the amine, known amount of diethanolamine was mixed with ten to fifteen times its molar concentration of alkaline chloramine-T and the reaction mixture was left for five days at room temperature, when the reaction was complete. The unconsumed oxidant was determined. It was found that the reaction can be represented by the equation :

$$\begin{aligned}4CH_3-C_6H_4-SO_2.N.NaCl \\ +NH(CH_2.CH_2.OH)_2+4H_2O \\ =2HCHO+2HCOOH+4CH_3.C_6H_4.SO_2.NH_2 \\ +NH_3+4NaCl \quad \ldots \quad (1)\end{aligned}$$

The products formaldehyde and formic acid were confirmed by usual tests. The formation of formaldehyde in the oxidation of the same substrate by the other oxidants, such as periodate, HOCl and ClO_2 has also been reported.[4,5] It has been examined qualitatively that formaldehyde is oxidised by chloramine-T, though the oxidation is very slow. From this it may be inferred that a part of the formaldehyde formed in the reaction is oxidised to formic acid.

The kinetic investigations were carried out at several initial concentrations of chloramine-T and amine at constant [OH⁻]. For each run a plot log a/(a-x) vs. time is straight line for nearly 60% of the reaction (Fig. 1). First order rate constants calcula-

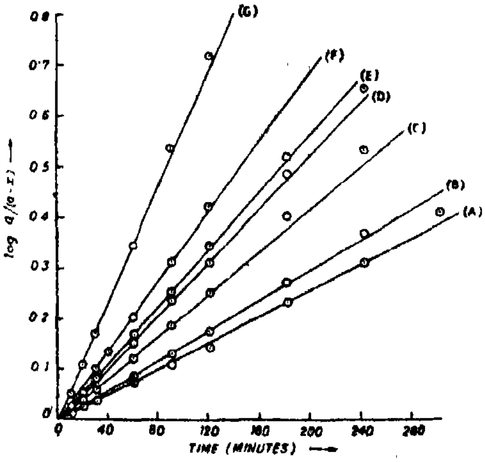


Fig. 1. Plot of log a/(a-x) vs. Time at 40°
[Chloramine-T] = 1.0 × 10⁻³ M, [NaOH] = 4.0 × 10⁻² M
[Diethanolamine] × 10³ M = 0.40(A), 0.50(B), 0.66(C), 0.80(D), 1.0(E), 1.25(F), 2.0(G)

ted from the equation $k = \frac{2.303}{t} \log a/(a-x)$ and also from the plot, log $a/(a-x)$ vs. time, agree closely with each other. The values of first order rate constants for a typical run at different temperatures are given in Table 1.

TABLE 1

EFFECT OF CHANGE OF TEMPERATURE

[Chloramine-T] = $1.0 \times 10^{-3} M$, [Diethanolamine] = $1.0 \times 10^{-2} M$
[NaOH] = $4.0 \times 10^{-3} M$

Temp.	40°	45°	50°	55°	60°
$k \times 10^{3}$ (min.$^{-1}$)	6.69	9.92	14.39	20.50	28.78

All subsequent investigations were also carried out with different concentrations of the amine, the other parameters being maintained constant. The rate constants, corresponding to different initial concentrations of the amine are summarised in Table 2.

TABLE 2

EFFECT OF VARYING [AMINE] ON THE RATE CONSTANT

[Chloramine-T] = $1.0 \times 10^{-3} M$, [NaOH] = $4.0 \times 10^{-3} M$; Temp = 40°

[Amine] $\times 10^{2} M$ =	0.40	0.50	0.66	0.80	1.0	1.25	2.0
$k \times 10^{3}$(min.$^{-1}$)	2.88	3.30	4.90	6.00	6.69	8.0	13.70

The first order rate constants are proportional to the concentration of the substrate. The reaction is, therefore, of first order with respect to diethanolamine.

The reaction has been studied at seven initial concentrations of the oxidant and it has been found that the first order constants remain unaltered, confirming that the reaction is first order in the oxidant. Table 3 shows the constants at different concentrations of the oxidant.

TABLE 3

EFFECT OF VARYING [CHLORAMINE-T] ON THE RATE CONSTANT

[Diethanolamine] = $1.0 \times 10^{-2} M$; [NaOH] = $4.0 \times 10^{-3} M$; Temp. = 40°

[Chloramine-T] $\times 10^{3} M$	0.60	0.80	1.0	1.25	1.50	2.0	2.50
$k \times 10^{3}$(min.$^{-1}$)	6.54	6.93	6.69	6.93	7.38	6.93	7.02

The rate study measurements, made at several [OH$^-$], exhibited a uniform decrease in the rate constant on increasing the [OH$^-$] of the media. The order in OH$^-$ ion is found to be nearly -1, as is evident from the following table.

TABLE 4

EFFECT OF VARYING [NaOH] ON THE RATE CONSTANT

[Chloramine-T] = $1.0 \times 10^{-3} M$; [Amine] = $1.0 \times 10^{-2} M$; Temp. = 40°

[NaOH] $\times 10^{3} M$	2.0	2.5	3.30	4.0	5.0	6.60
$k \times 10^{3}$(min.$^{-1}$)	13.4	10.28	8.59	6.69	5.53	3.38
$k \times$ [NaOH] $\times 10^{5}$	2.68	2.57	2.83	2.67	2.76	2.25

Salts like, NaCl, KCl, CH_3COONa and K_2SO_4 are found to have negligible effect on the reaction rates.

The rates were also studied at different water-methanol mixtures. It is observed that an increase in methanol concentration slightly retards the rate of the reaction (e.g., $k = 6.69 \times 10^{-3}$ (min.$^{-1}$) at 0% methanol and $k = 4.328 \times 10^{-3}$ (min.$^{-1}$) at 25% methanol).

Arrhenius parameters were also calculated from the rate study measurements carried out at five different temperatures.

TABLE 5

ARRHENIUS PARAMETERS IN THE CHLORAMINE-T OXIDATION OF DIETHANOLAMINE

E_A(K cal/mole)	log A	ΔH^{*}(K cal/mole)	ΔS^{*}(e.u.)
14.64	6.267	14.02	-31.85

Discussion :

In aqueous solution, chloramine-T hydrolyses as follows :

$$CH_3.C_6H_4.SO_2.N.NaCl + H_2O \rightleftharpoons CH_3.C_6H_4.SO_2.N.HCl + NaOH \quad \dots (2)$$

$$CH_3.C_6H_4.SO_2.N.HCl + NaOH \rightleftharpoons CH_3.C_6H_4.SO_2.NH_2 + Na^{+} + ClO^{-} \quad \dots (3)$$

The various oxidising species may be chloramine-T itself, *p*-toluenesulphochloramide and hypochlorite ion. As the rate is decreased on increasing [OH$^-$], *p*-toluenesulphochloramide is undoubtedly the main oxidising species[6].

It is proposed that the amine molecule reacts in a slow step with *p*-toluenesulphochloramide to form an intermediate compound which subsequently interacts with another molecule of *p*-toluenesulphochloramide in a fast step yielding formaldehyde. The steps thus involved are

$$CH_3.C_6H_4.SO_2.N.NaCl + H_2O \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} CH_3.C_6H_4.SO_2.N.HCl + NaOH \quad \dots (4)$$

$$CH_3.C_6H_4.SO_2.N.HCl + NH(CH_2.CH_2.OH)_2 \xrightarrow[\text{(slow)}]{k'_2} CH_3.C_6H_4.SO_2.NH_2 + NCl(CH_2.CH_2.OH)_2 \quad \dots (5)$$

$$NCl(CH_2.CH_2.OH)_2 + CH_3.C_6H_4.SO_2.N.HCl + 2H_2O \underset{\text{(fast)}}{\overset{k'_3}{\rightleftharpoons}} 4HCHO + CH_3.C_6H_4.SO_2.NH_2 + NH_3 + 2HCl \quad \dots (6)$$

Applying steady state treatment to the intermediates with the reasonable approximation that

$k'_{-1} \gg k'_2$ so that k'_{-1} [NaOH] $\gg 2k'_2[NH(CH_2.CH_2.OH)_2]$, the rate law is given by

$$-\frac{d}{dt}[\text{Chloramine-T}] = \frac{2k'_1\, k'_2[\text{Chloramine-T}][NH(CH_2.CH_2.OH)_2]}{k'_{-1}[NaOH]} \quad \ldots \quad (7)$$

which is consistent with the experimental observations.

The deviation of order in alkali from −1 is explained by an insignificantly small fraction of the overall reaction to proceed via an intermediate path involving interaction of hypochlorite ion[7] in steps (5) and (6). The rate law in this case is obtained as

$$-\frac{d}{dt}[\text{Chloramine-T}] = 2k'_2[\text{Chloramine-T}][NH(CH_2.CH_2.OH)_2] \quad \ldots \quad (8)$$

showing the rate to be independent of $[OH^-]$.

A slight decrease in the rate constant on addition of methanol is in confirmity with this alternative path.

The negative value of entropy of activation is explained by the proposed mechanism, e. g., the water molecule has been incorporated in the reaction sequence and this tends to decrease in entropy[8].

Thus it may be concluded that chloraminometric oxidation of diethanolamine proceeds via two paths, one involving interaction of *p*-toluenesulphochloramide and the other of hypochlorite ion with diethanolamine in the rate determining step, the former being principally predominant.

According to the mechanism suggested, two moles of chloramine-T should be consumed for each mole of the amine, but the stoichiometric investigations show that four moles of chloramine-T are consumed. Hence, it seems possible that half of the formaldehyde, formed in the reaction mixture, is oxidised into formic acid in the presence of excess of the oxidant.

$$NH(CH_2.CH_2.OH)_2 + 2CH_3.C_6H_4.SO_2.N.NaCl + 2H_2O = 4HCHO + 2CH_3.C_6H_4.SO_2.NH_2 + NH_3 + 2NaCl \quad \ldots \quad (9)$$

$$2HCHO + 2CH_3.C_6H_4.SO_2.N.NaCl + 2H_2O = 2HCOOH + 2CH_3.C_6H_4.SO_2.NH_2 + 2NaCl \quad \ldots \quad (10)$$

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Kinetics of Silver(I)-Catalysed Oxidation of Some Aromatic Azo Compounds by Peroxydisulphate

P. S. N. MURTY and P. V. SUBBA RAO*

Department of Chemistry, Andhra University, Waltair

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The kinetics of oxidation of some aromatic azo compounds by peroxydisulphate catalysed by silver(I), was investigated. The reaction is first order with respect to peroxydisulphate and silver(I) and zero order in each of the azo compounds. The reaction exhibits induction period which decreases with increasing silver(I) concentration. Increase in ionic strength decreases the rate. The reaction mixture initiates vinyl polymerization.

THE kinetics of peroxydisulphate oxidation of a number of organic and inorganic substrates has been reported and reviewed.[1,2] However, a survey of the literature has shown that the kinetics of oxidation of azo compounds by peroxydisulphate has not been made so far. Hence a detailed kinetic study of the oxidation of some aromatic azo compounds by peroxydisulphate catalysed by silver(I) seemed desirable. A separate investigation has shown that the uncatalysed oxidation is very slow under the experimental conditions employed. The results indicate a radical chain mechanism.

Experimental

All the azo compounds used were twice recrystallised. All the other materials used were of analytical reagent grade. The azo compounds studied are pink in aqueous acid solution. For example, methyl orange and methyl red have pK values 3.4 and 5.0 respectively and hence in acid medium these two would exist in protonated form. The course of the reaction was followed by measuring the optical density of the unreacted compound in aqueous sulphuric acid medium using a green filter (500-530 nm). The ionic strength was maintained constant with sodium bisulphate. Under these conditions Beer's Law was obeyed by each of the azo compounds and all the other materials concerned have negligible absorption. Under the experimental conditions employed for the catalysed reaction, the rate of uncatalysed reaction was found to be negligibly small in comparison with the rates of the catalysed reaction just at the end of the induction period (Table 1). Hence no correction has been applied for uncatalysed reaction while analysing the rate data.

Stoichiometry : The stoichiometry of the reaction was investigated by the addition of a known excess of the azo compound to peroxydisulphate in 1 *N* H_2SO_4, 2.4×10^{-3} *M* $AgNO_3$ and 8% V/V acetic acid solution. The amount of the azo compound consumed was calculated from the decrease in the optical density after the completion of the reaction (which is indicated by the constancy of the optical

TABLE 1

COMPARISON OF RATES OF SILVER(I)-CATALYSED AND UNCATALYSED OXIDATIONS

$[S_2O_8^{=}]=5.0\times10^{-3}$ *M*, $[H^+]=1.0$ *M* [HoAc]=1.6% V/V ; Temp.$=30\pm0.1°$ $\mu=3.02$

Substrate	[Substrate] $\times10^5$ *M*	$k_0\times10^7$ moles. lit^{-1}. min^{-1} of the catalysed reaction in the presence of $[Ag^+]=8.0\times10^{-4}M$.	$k_0\times10^{10}$ moles. lit^{-1}. min^{-1} of the uncatalysed reaction.
[4]-chloro-Benzol-azo-[4']-dimethyl aniline [4, 4' $Cl-C_6H_4-N=N-C_6H_4-N(CH_3)_2$]	2.42	2.70	9.23
[4]-nitro-Benzol-azo-[4']-dimethyl aniline [4, 4' $NO_2-C_6H_4-N=N-C_6H_4-N(CH_3)_2$]	2.50	3.35	7.94
[4']-Dimethyl-amido-azo-Benzol-[4]-Sulphonic acid (Methyl Orange) [4, 4' $HSO_3-C_6H_4-N=N-C_6H_4-N(CH_3)_2$]	2.08	8.10	8.32
[4]-Dimethyl amido-azo-Benzol-[2]-mono carboxylic acid (Methyl Red) [2, 4 $COOH-C_6H_4-N=N-C_6H_4-N(CH_3)_2$]	1.24	5.26	5.67

density with time). It was found that for all the aromatic azo compounds studied, 1 mole of the azo compound was found to consume 1 mole of peroxydisulphate. Under the experimental conditions employed acetic acid is not oxidised by peroxydisulphate.

Products of the reaction: The stoichiometry indicates the formation of azoxy compound as the product of the oxidation. This was confirmed by comparing this product with the oxidation product obtained by reaction with hydrogen peroxide, which was earlier reported[9] to be an azoxy compound. The identity was established by Co T.L.C and superimposable I.R. spectra of these two products. The I.R. spectrum of the product has shown that $-N(CH_3)_2$ group is not affected thereby proving that the site of attack is $-N=N-$ group.

Results

Several kinetic runs were carried out for the oxidation of each of the azo compounds studied, keeping the concentration of peroxydisulphate at least fifty times that of the concentration of azo compound. The plot of optical density versus time for a typical azo compound has been shown in Fig. 1. A straight line is obtained only for the latter part of the reaction. The reaction seems to have an induction period. The linear dependence of the optical density on time after the induction period shows that the reaction is zero order with respect to each of the azo compounds (Fig. 1). The pseudo zero order rate constant k_0 was calculated from the slopes of these straight lines. It is also evident from the figure that the induction period decreases with increasing Ag(I) concentration. A similar behaviour was also observed in the oxidation of other azo compounds. The rates were also determined for different initial concentrations of each of the azo compounds keeping the concentrations of all the other materials constant. The data were presented in Table 2. It is evident from the data that the rate of the reaction is independent of the concentration of the azo compound showing the zero order kinetics with respect to the azo compound.

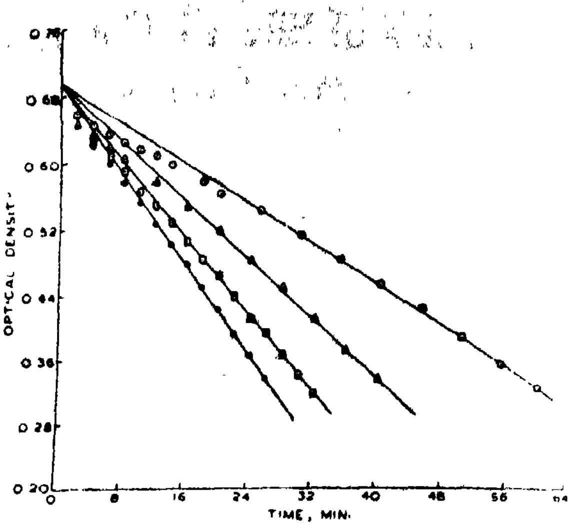


Fig. 1. Zero-Order dependence of rate on the concentration of azo compound.
$[4,4'Cl-C_6H_4-N=N-C_6H_4-N(CH_3)_2]=2.42\times10^{-4}$ M. $[H^+]=1.0$ M $[S_2O_8^{=}]=2.0\times10^{-2}$ M [HoAC]=1.6% V/V
Temperature $=30\pm0.1°$ $\mu=3.01$
○—○ $[Ag(I)]=1.6\times10^{-4}M$ △—△ $[Ag(I)]=2.4\times10^{-4}M$
▣—▣ $[Ag(I)]=3.2\times10^{-4}M$ ●—● $[Ag(I)]=4.0\times10^{-4}M$

TABLE 2

ZERO-ORDER DEPENDENCE OF RATE ON THE CONCENTRATION OF AZO COMPOUND

$[S_2O_8^{=}]=3.5\times10^{-2}$ M; $[H^+]=1.0$ M; [HoAc]=2.4% V/V; Temp. $=30\pm0.1°$ $\mu=3.02$

Substrate	[Substrate] × 10^4 M	[Ag^+] × 10^4 M	Rate × 10^7 moles. lit^{-1}. min^{-1}
[4]-chloro-	1.82	2.4	5.58
Benzol-azo-	2.42	2.4	5.58
[4']-Dimethyl	3.03	2.4	5.58
aniline			
$[4,4'Cl-C_6H_4-N=N-C_6H_4-N(CH_3)_2]$			
[4]-nitro-	1.25	1.6	4.56
Benzol-azo-	1.88	1.6	4.56
[4']-Dimethyl	2.50	1.6	4.57
aniline			
$[4,4'NO_2-C_6H_4-N=N-C_6H_4-N(CH_3)_2]$			
[4']-Dimethyl-	2.08	0.8	4.80
amido-azo-	2.60	0.8	4.80
Benzol-[4]-	3.12	0.8	4.79
Sulphonic acid			
(Methyl Orange)			
$[4,4'HSO_3-C_6H_4-N=N-C_6H_4-N(CH_3)_2]$			
[4]-Dimethyl-	0.74	0.8	3.48
amido-azo-	1.24	0.8	3.48
Benzol-[2]-	1.73	0.8	3.48
mono carboxylic acid			
(Methyl Red)			
$[2,4\ COOH-C_6H_4-N=N-C_6H_4-N(CH_3)_2]$			

The value of k_0 was also determined at different peroxydisulphate concentrations, for the oxidation of each of the azo compounds. Plot of k_0 versus $[S_2O_8^=]$ is a straight line passing through the origin. This shows that the reaction is first order with respect to peroxydisulphate in all the cases (Fig. 2).

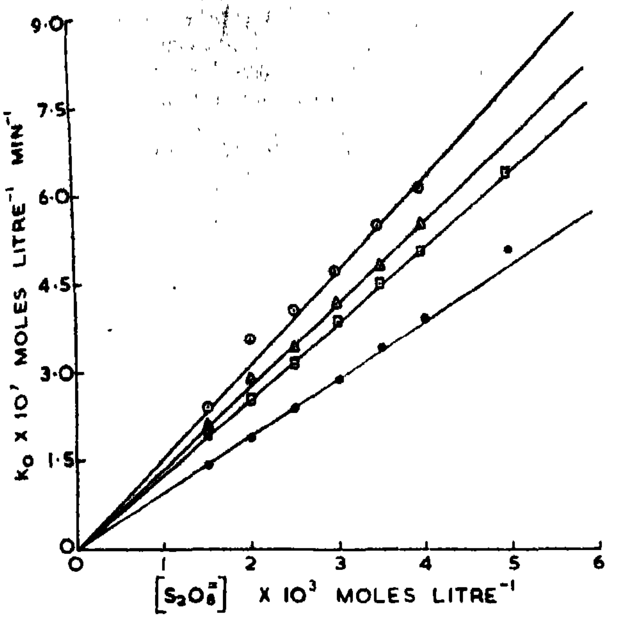


Fig. 2. First Order dependence of rate on the concentration of $S_2O_8^=$

○—○ $[Ag(I)] = 2.4 \times 10^{-4} M$
$[4, 4'Cl-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 2.42 \times 10^{-4} M$

⊡—⊡ $[Ag(I)] = 1.6 \times 10^{-4} M$
$[4, 4'NO_2-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 2.50 \times 10^{-4} M$

△—△ $[Ag(I)] = 8.0 \times 10^{-4} M$
$[4, 4'HSO_3-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 2.08 \times 10^{-4} M$

●—● $[Ag(I)] = 8.0 \times 10^{-4} M$
$[2, 4COOH-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 1.24 \times 10^{-4} M$

$[H^+] = 1.0\ M$; $[HoAC] = 1.6\%$ V/V ; $\mu = 3.02$
Temp. $= 30 \pm 0.1°$

The value of k_0 was determined at different Ag(I) concentrations. A plot of k_0 versus [Ag(I)] is a straight line passing through the origin, showing that the reaction is first order with respect to Ag(I) (Fig. 3). This also shows that the extent of uncatalysed reaction is negligibly small. In view of all the above facts, the experimental rate law may be expressed as

$$\frac{-d}{dt}[\text{azo compound}] = k\,[S_2O_8^=]\,[Ag^+]$$

Effect of Ionic Strength: The reaction was studied at different ionic strengths by varying the concentration of sodium perchlorate. The increase in ionic strength produced a decrease in the rate of the reaction. A plot of log k_0 versus $\sqrt{\mu}$ is a straight line with a negative slope.

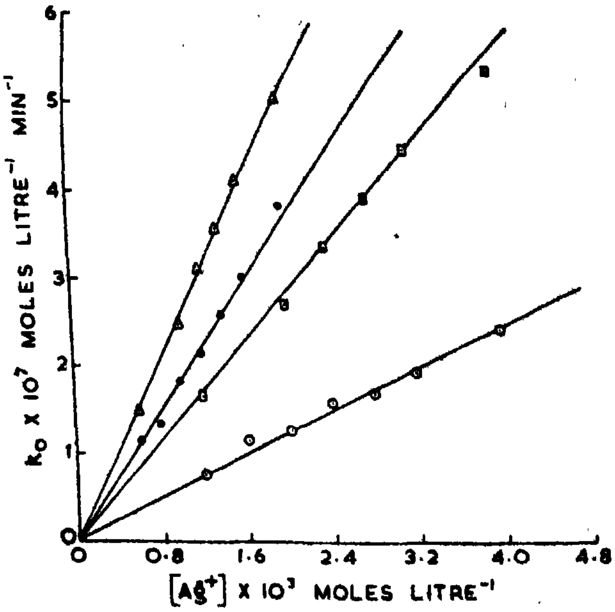


Fig. 3. First Order dependence of rate on the concentration of Ag(I)

$[S_2O_8^=] = 1.0 \times 10^{-3} M$
$[4, 4'Cl-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 2.42 \times 10^{-4} M$
$[S_2O_8^=] = 2.0 \times 10^{-3} M$
$[4, 4'NO_2-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 2.50 \times 10^{-4} M$
$[S_2O_8^=] = 1.50 \times 10^{-3} M$
$[4, 4'HSO_3-C_6H_4-N=N-C_6H_4-N(CH_3)_2 = 2.08 \times 10^{-4} M$
$[S_2O_8^=] = 1.60 \times 10^{-3} M$
$[2, 4COOH-C_6H_4-N=N-C_6H_4-N(CH_3)_2] = 1.24 \times 10^{-4} M$
$[H^+] = 1.0\ M$; $[HoAC] = 1.6\%$ V/V, $\mu = 3.01$; Temp. $= 30 \pm 0.1°$

Effect of Acrylonitrile: The reaction mixture with acrylonitrile yielded a white precipitate showing that the reaction initiates vinyl polymerization. Further, the rate measurements before the solid polymer formation have shown that an increase in acrylonitrile concentration reduced the rate of oxidation of azo compounds (Table 3). This is due to the well known effect of acrylonitrile as a scavenger of free radicals, resulting in the inhibition. Thus free radicals seem to be involved in the reaction.

Mechanism :

The observed rate-law $\frac{-d}{dt}$ [azo compound] $= k[S_2O_8^=][Ag^+]$ suggests that the rate determining step involves Ag^+ and $S_2O_8^=$. This coupled with the observed induction period for the reaction as well as the evidence obtained for free radical formation is suggestive of a chain mechanism.

$$Ag^{+}+S_2O_8^{=}\xrightarrow{k_1}Ag^{2+}+SO_4^{-}+SO_4^{=}$$

$$Ag^{2+}+-N=N-\xrightarrow{k_2}\left[-\dot{N}-\overset{+}{N}-\right]+Ag^{+}$$
$$\qquad\qquad\qquad\qquad(X)$$

$$\underset{(X)}{\left[-\dot{N}-\overset{+}{N}-\right]}+S_2O_8^{=}\xrightarrow[H_2O]{k_3}-N=\overset{+}{\underset{O^-}{\underset{|}{N}}}-+SO_4^{-}+SO_4^{=}+2H^{+}$$

$$Ag^{+}+SO_4^{-}\xrightarrow{k_4}Ag^{2+}+SO_4^{=}$$

$$SO_4^{-}+\underset{(X)}{\left[-\dot{N}-\overset{+}{N}-\right]}\xrightarrow[H_2O]{k_5}-N-\overset{+}{\underset{O^-}{\underset{|}{N}}}\;+SO_4^{=}+2H^{+}$$

The application of steady state approximation to SO_4^{-}, X and Ag^{2+} leads to the rate law

$$\frac{-d}{dt}[\text{azo compound}]=[Ag^{+}][S_2O_8^{=}]\left\{k_1+\frac{k_1k_3k_4}{k_5}\right\}^{1/2}$$

which is in agreement with the experimental rate law. It is interesting to note that a similar kinetic pattern were reported in Ag(I)-catalysed peroxydisulphate oxidation of methanol[4], ethanol[4], glycol[5], lactic acid[6], glycerol[7], propyonaldehyde[8] and urea[9]. In all these cases the first order kinetics was observed with respect to peroxydisulphate and silver(I) and zero order kinetics with respect to the reductant. A similar chain mechanism has been proposed to account for the observed results.

TABLE 3

INFLUENCE OF ACRYLONITRILE CONCENTRATION ON RATE

$[S_2O_8^{=}]=2.0\times10^{-2}\,M$, $\mu=3.02$; $[Ag^{+}]=2.0\times10^{-3}\,M$; $[H^{+}]=0.25\,M$; [HoAc] = 1.6% V/V ; Temp. = 30 ± 0.1°

Substrate	[Substrate] × 10^4 *M*	[Acrylonitrile] *M*	$k_0\times10^7$ moles.lit^{-1}.min^{-1}
[4]-chloro-	2.42	0.30	1.22
Benzol-azo-	2.42	0.60	1.10
[4']-Dimethyl	2.42	0.90	0.87
aniline	2.42	1.21	0.64
[4, 4' Cl—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]			
[4]-nitro-	2.50	0.30	2.64
Benzol-azo-	2.50	0.60	1.89
[4']-Dimethyl	2.50	0.90	1.23
aniline	2.50	1.21	0.87
[4, 4' NO_2—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]			
[4']-Dimethyl-	2.08	0.30	5.05
amido-azo-	2.08	0.60	4.57
Benzol-[4]-	2.08	0.90	2.93
Sulphonic acid	2.08	1.21	2.18
(Methyl Orange)			
[4, 4' HSO_3—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]			
[4]-Dimethyl-	1.24	0.30	3.58
amido-azo-	1.24	0.60	2.93
Benzol-[2]-	1.24	0.90	2.17
mono carboxylic	1.24	1.21	2.15
acid (Methyl Red)			
[2, 4 COOH—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]			

TABLE 4

ACTIVATION PARAMETERS

Temp. = 30 ± 0.1°

Substrate	E K cal.mole^{-1}	$\Delta S^{\neq}$ cal.deg^{-1}.mole^{-1}
[4]-chloro-Benzol-azo-[4']-Dimethyl aniline [4, 4' Cl—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]	11.3	−48.8
[4]-nitro-Benzol-azo-[4']—Dimethyl aniline [4, 4' NO_2—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]	13.8	−40.9
[4']-Dimethyl-amido-azo-Benzol-[4]-Sulphonic acid (Methyl Orange) [4, 4' HSO_3—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]	5.2	−69.9
[4]-Dimethyl-amido-azo-Benzol-[2]-mono carboxylic acid (Methyl Red) [2, 4 COOH—C_6H_4—N=N—C_6H_4—$N(CH_3)_2$]	9.6	−54.7

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Kinetics and Mechanism of Halogenation Reactions Involving Some Aromatic Primary Amines (Part II)

P. S. RADHAKRISHNAMURTI* and M. D. PRASAD RAO

Department of Chemistry, Berhampur University, Berhampur-7 (Orissa)

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Kinetics of the reactions of aniline and a few substituted anilines with CAT in aqueous acetic acid-$HClO_4$ mixtures and in aqueous acetic acid and sodium acetate buffers is reported. The reactions are first order in CAT and first order in the aromatic base. The reactions are faster in aqueous acetic acid-sodium acetate buffer than in aqueous acetic acid-$HClO_4$ mixtures for all amines except for paranitro aniline. This confirms our earlier finding that it is the free base which reacts for all amines except for *p*-nitro aniline where the protonated form is the reactive species. A competition between the protonation process and the effect of dielectric constant of the system on the reaction rate is observed at an above 0.025 *M* $HClO_4$. Kendall's treatment has been applied to compute the acid independent rate constants which have been used for comparison of structure and reactivity.

IN our previous communication[1] we have shown that chloramine-T(CAT) chlorinates aniline, *p*-chloro aniline, *p*-toluidine and *p*-nitro aniline at measurable rates and evidences were presented for direct halogen transfer. The present communication is concerned with kinetics of chlorination of aniline, *o*-chloro-aniline, *o*-toluidine, *m*-chloro aniline and *m*-toluidine by chloramine-T in aqueous acetic acid.

Materials and Methods :

Chloramine-T of M & B make of AR grade was used without further purification. *o*-chloro aniline, *o*-toluidine, *m*-chloro aniline and *m*-toluidine were of BDH AR grade and were distilled before use. The disappearance of CAT was estimated by standard iodometric method. The rate constants have been computed by the usual tangential method.

Stoichiometry :

Stoichiometry of the reaction was studied by taking the substrate in excess as well as by taking the CAT in excess ; the former to judge the reaction steps during kinetic runs and the latter to judge the overall reaction products. The equivalence of CAT per mole of substrate in the two cases has been found to be 1 and 2 respectively. Thus the reaction under conditions of kinetic run can be represented as :

$$C_6H_5NH_2+CH_3\ C_6H_4SO_2\ N\ NaCl+H_2O \longrightarrow C_6H_4Cl\ NH_2+CH_3C_6H_4SO_2NH_2+NaOH.$$

On the other hand, the overall reaction with excess of CAT proceeds further to halogenate the mono-chloro product and hence the reaction is :

$$C_6H_5NH_2+2CH_3C_6H_4SO_2\ N\ NaCl+2H_2O \longrightarrow C_6H_3Cl_2NH_2+2CH_3C_6H_4SO_2NH_2+2\ NaOH$$

the yields of isolated monochloroanilines under the experimental conditions were greater than 80%.

Results and Discussion :

In the concentration range employed in the study the reactions are second order : first order in the substrate and first order in the halogenating agent. The earlier idea that aromatic chlorination is zero order in the substrate[2] does not seem to hold good, as the first order rate constant increases with increasing concentration of the substrate confirming the first order nature with respect to the substrate (Table 1). Variation of CAT in the concentration

TABLE 1

10% AQUEOUS ACETIC ACID, 0.0125 *M* $HClO_4$, CAT=0.00045 *M*, TEMP 35°

Substrate	Concentration of substrate	k_1	k_2 l.mole^{-1} sec^{-1}
Aniline	0.004512	0.0007334	0.1625(0.08125)
	0.005951	0.0009438	0.1585(0.07925)
	0.007161	0.001151	0.1607(0.08035)
o-cl. aniline	0.002391	0.0004411	0.1840
	0.005684	0.001106	0.1945
	0.007728	0.001431	0.1852
m-toluidine	0.002339	0.0004217	0.1807
	0.005461	0.001009	0.1849
	0.007747	0.001502	0.1938

range studied yields a constancy in the first order rate constant indicating the dependence on CAT as unity (Table 2).

TABLE 2

ANILINE=0.005156 *M*. 10% HAc, 0.0125 *M* $HClO_4$. TEMP 35°.

CAT	k_1 sec^{-1}
0.0002111	0.0008026
0.0004500	0.0008172
0.0007188	0.0007723

Effect of acidity :

There is inverse dependence on acidity as compared to direct dependence in the case of *p*-nitroaniline. The differential dependence on acidity in the case of compounds under present study and *p*-nitroaniline is an important observation and is a pointer to the nature of the substrate species taking part in the reaction. It appears that the reactive species in the case of *o*-chloroaniline, *o*-toluidine, *m*-chloroaniline, *m*-toluidine is the unprotonated amine whereas it is the protonated form for *p*-nitroaniline. Such reasoning has been done earlier by Bell.[3] (Table 3).

TABLE 3

10% AQUEOUS ACETIC ACID, CAT=0.00045*M*, TEMP 35°.

Substrate	k_2 1.mole^{-1} sec^{-1} H$^+$=0.00606*M*	H$^+$=0.0125*M*	H$^+$=0.025*M*	H$^+$=0.05*M*
o-cl. aniline	0.2698	0.1945	0.1694	0.1090
o-toluidine	0.2291	0.1610	0.1292	0.06757
m-cl aniline	0.2099	0.1672	0.1212	0.08079
m-toluidine	0.2878	0.1849	0.1119	0.05343

Solvent effect :

Increasing acetic acid percentage decreases the rate and also increase in ethanol percentage decreases the rate, pointing to the fact that it is dipole-dipole reaction between CAT and amines. Plot of $\log_{10} k_2$ vs 1/D and $\log_{10} k_2$ vs D-1/2D+1 are linear (Table 4 & 5).

TABLE 4

$HClO_4$=0.0125 *M*, CAT=0.00045 *M*, Temp. 35°.

Substrate	k_2 1.mole^{-1} sec^{-1} 10% AcOH	20% AcOH	30% AcOH	50% AcOH
o-cl. aniline	0.1945	0.1832	0.1272	0.08455
o-toluidine	0.1610	0.1305	0.09954	0.04308
m-chloro aniline	0.1672	0.1351	0.07848	0.05340
m-toluidine	0.1849	0.1072	0·07065	0.0385

TABLE 5

CAT=0.00045*M*, $HClO_4$=0.0125 *M*, Temp. 35°.

Substrate	k_2 1.mole^{-1} sec^{-1} 10% EtOH	20% EtOH	30% EtOH
Aniline	0.1470	0.08714	0.05453
p-nitro aniline	0.01976	0.01391	0.0061

Structure-Reactivity :

In our previous work with aniline, *p*-chloro aniline, *p*-bromo aniline, *p*-iodo aniline, *p*-toluidine and *p*-nitro aniline, we have shown that *p*-nitro aniline reacts slower and *p*-halogeno amines and *p*-toluidine react faster. In all the cases the products are ortho chloro isomers. In case of aniline the isomer distribution is equal, the products being both para and ortho chloro isomers. Hence to compare the reactivity of the unsubstituted derivative the rate constant is divided by a statistical factor 2 to give the partial rate with respect to ortho isomer. In the present study the reactivities of *o*-chloro aniline and *o*-toluidine are slightly higher than *p*-chloro aniline and *p*-toluidine. *m*-chloro aniline and *m*-toluidine exhibited higher reactivity as compared to the *p*-chloro aniline and *p*-toluidine. In case of meta substituted anilines two nuclear positions are available for halogenation. Hence k'_2 (Ortho) (partial rate) is computed by dividing the observed rate by a statistical factor 2. The partial rates for aniline and meta substituted anilines when taken into consideration give a clear picture of reactivity (Table 6).

TABLE 6

10% AQUEOUS ACETIC ACID 0.0125 *M*, $HClO_4$
CAT=0.00045 *M*, TEMP. 35°.

Substrate	k_2 1.mole^{-1} sec^{-1}	Substrate	k_2 1.mole^{-1} sec^{-1}
Aniline	0.1625(0.08125)	*o*-cl.aniline	0.1945
p-cl. aniline	0.1432	*m* cl.aniline	0.1672(0.0836)
p-bromo aniline	0.1865	*o*-toluidine	0.1610
p-iodo aniline	0.3479	*m*-toluidine	0.1849(0.0924)
p-toluidine	0.1486	*p*-nitro aniline	0.02500

Comparison of rates in pure aqueous medium and in aqueous acetic acid medium at different concentrations of perchloric acid :

It is observed that with increasing percentages of acetic acid the rate decreases. Increasing percentage of acetic acid decreases the dielectric constant of the medium. Decrease in dielectric constant decreases the rate. But increase in dielectric constant increases the rate at constant acidity till 0.0125 *M*. But at 0.025 *M* and 0.05 *M* acidities there is near equivalence in rate with increase in dielectric constant. This near equivalence in rate at and above 0.025 *M* $HClO_4$ is much against the dependence of rate on dielectric constant of the system for dipole-dipole reactions. This requires explanation in the two competing processes (1) Increase in rate due to increase in dielectric constant of the system ; (2) Decrease in rate due to increasing the acidity ; the second factor seems to predominate at higher acidities thus leading to an apparent decrease in rate (Table 7).

TABLE 7

SUBSTRATE , ANILINE=0.005 *M*, CAT=0.00045 *M*,
TEMP 35°.

H$^+$ M	k_2 1.mole^{-1} sec^{-1} Aqueous medium	10% AcOH	20% AcOH	30% AcOH	50% AcOH
0.00603	0.7565	0.2245	0.1508	0.1186	0.0627
0.0125	0.2519	0.1625	0.1128	0.08567	0.05643
0.025	0.09642	0.1052	0 05737	0.04315	0.01879
0.05	0.06697	0.06846	0.03196	0.02221	0.01280

Effect of change of pH :

The system was changed to aqueous acetic acid-

sodium acetate buffer from aqueous aceiic acid-$HClO_4$ to prove that it is the unprotonated amine which participates as compared to the protonated form of the *p*-nitro aniline. Reactions have been conducted in various percentages of acetic acid and sodium acetate buffers. Reactions are faster in all the cases except *p*-nitro aniline where retardation is observed as compared to the rates of aqueous acetic acid-$HClO_4$ mixtures. The extent of protonation will be less in aqueous acetic acid-sodium acetate buffer as compared to protonation in aqueous acetic acid-$HClO_4$ medium. This confirms our finding reported by us[1] that there is inverse dependence on acid for all amines except *p*-nitroaniline for which there is direct dependence on acid. Hence all the amines reacted faster as the free amine concentration increased whereas in the case of *p*-nitroaniline the protonated form which is the reactive species decreases due to less acidic system and hence retardation in rate (Table 8).

TABLE 8

CAT=0.00045 *M*, Temp. 35°.

Substrate	k_2 l.mole^{-1} sec^{-1} 20% AcOH 0.02 *M* AcONa	50% AcOH 0.02 *M* AcONa	90% AcOH 0.02 *M* AcONa
Aniline	0.3723	0.2629	0.0588
p-cl. aniline	0.8905	0.1975	0.0465
p-bromo aniline	0.4985	0.2194	0.05876
p-iodo aniline	0.6676	0.4566	0.07736
p-toluidine	0.4957	0.1892	0.0464
p-nitro aniline	0.009714	0.003695	0.00107

Ionic Strength Effect :

Increasing the concentration of $NaClO_4$ does not effect the rate appreciably indicating that ionic strength effect is negligible. Further, addition of KCl in place of $NaClO_4$ does not alter the rate. The salt effects observed are in consonance with the dipole-dipole reactions (Table 9).

TABLE 9

CAT=0.00045 *M*, 10% ACETIC ACID, 0.0125 *M*, $HClO_4$, TEMP 35°. ANILINE=0.005146 *M*

Salt	Concentration	k_2 l.mole^{-1} sec^{-1}
	0.0025	0.1363
$NaClO_4$	0.005	0.1336
	0.0075	0.1336
KCl	0.00063	0.1463

Application of Kendall's treatment :

Structure reactivity relationship can be better understood by the application of Kendall's treatment[4] which envisages the computation of true acidity independent rate constants. The free base will exist in equilibrium with its conjugate acid ion as shown in the equation :

$$R\ NH_2 + H_3O^+ \rightleftharpoons R\ NH_3^+ + H_2O$$

Applying the Hammett acidity function h_0 the concentration of the free base [B] at equilibrium can be calculated from $\log [B] = h_0 - Pka + \log [BH^+]$ where Pka is the dissociation constant of the conjugate acid. Because the acid is in excess, the concentration of $[BH^+]$ can be assumed to be constant and may be taken as equal to stoichiometric amount of the base added. The first order rate constants that are obtained at different acidities, when divided by the respective effective concentrations at equilibrium, yielded second order rate constants which are very close to each other within the limits of experimental errors and with in the limitations involved in employing the treatment. The acid independent rate constants are recorded in Table 10.

TABLE 10

10% AQUEOUS ACETIC ACID, CAT=0.00045 *M*, TEMP. 35°.

Substrate	k_2 l.mole^{-1} sec^{-1} H^+=0.006*M*,	H^+=0.0125*M*,	H^+=0.025*M*,	H^+=0.05*M*,
o-cl. aniline	1.782	1.581	1.991	3.415
m-cl. aniline	10.28 (5.14)*	9.126 (4.563)*	10.55 (5.27)*	14.7 (7.35)*
o-toluidine	301.9	261.0	302.8	331.0
m-toluidine	228.7 (114.35)*	180.7 (90.35)*	158.1 (79.05)*	220.4 (110.2)*

* represents k'_2 (Partial rate)

With the acid independent rate constants the order of reactivity is :

o-toluidine > *m*-toluidine > *m*-chloroaniline > *o*-chloroaniline. It is clear that the application of the treatment is quite successful for even halogenation reactions which has been tried for the first time though it has been employed for other processes[5].

To investigate the effect of temperature and to evaluate various thermodynamic parameters, measurements were made at 25°, 30° and 35°. The results obtained for aniline at 35° are summarised in Table 11.

TABLE 11

THERMODYNAMIC PARAMETERS FOR ANILINE

Substrate	E (K.cal.)	ΔH (K.cal)	$\log_{10}A$	$\Delta S^{\neq}$ (eu)
Aniline	18.31	17.69	14.76	−4.65

Of the various species of CAT, *p*-toluene sulphochloramide ($CH_3C_6H_4SO_2NHCl$) produced from CAT in a fast step is considered to be the active species under the experimental conditions. The *p*-toluene sulphochloramide produced in the fast step reacts in a slow step with the free base in case of substrates studied other than *p*-nitro aniline to give the products.

$$H_3SO_2N\ NaCl + H_2O \overset{k_1}{\rightleftharpoons} CH_3C_6H_4SO_2NHCl + NaOH$$

$$RNH_2 + H^+ \overset{k_2}{\rightleftharpoons} RNH_3^+$$

$$H_2 + CH_3C_6H_4SO_2NHCl \xrightarrow[slow]{k_3} RCl\ NH_2 + CH_3C_6H_4SO_2\ NH_2$$

$(RNH_2)_T = RNH_2 + RNH_3^+$ so $RNH_2 = (RNH_2)_T'/\{1 + k_2H^+\}$

ting for RNH_2 which is the reactive species

$$\frac{-d(CAT)}{dt} = \frac{k_1 k_3 (RNH_2)_T (CAT)}{(1 + k_2H^+)} \quad \ldots \quad (1)$$

stituting for the reactive species RNH_3^+ for *p*-nitroaniline $RNH_3^+ = k_2(RNH_2)(H^+)$ accordingly the rate law for *p*-nitroaniline can be

$$\frac{-d(CAT)}{dt} = k_1 k_2 k_3 (RNH_2)(CAT)(H^+) \quad \ldots \quad (2)$$

The rate laws (1) and (2) are quite in agreement with the experimental results.

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Resin Catalysed Hydrolysis of Formamide

UMAKANT SENTIYA* and R. P. SHUKLA**

Department of Applied Chemistry, Government Engineering College, Jabalpur, M. P.

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Kinetics of the reaction between resin and formamide have been studied at different temperatures. The rate of the reaction has been followed by conductance measurements. The reaction has been found to be first order with respect to formamide and independent to resin concentration. The rate constant increase with an increase in resin concentration and attains optimum value. Arrhenius parameters and kinetic order support a unimolecular nucleophilic attack of water molecule on the conjugate acid species of formamide.

HE acid catalysed hydrolysis of amides[1-16] specially formamide has been studied by number workers[17] and shown to involve a unimolecular ıechanism. Further these exhibit rate maxima 'hich have generally been considered to arise ecause once the amide is fully protonated a further ıcrease in acid concentration merely decreases the ater activity.[9] In view of the various suggestions nd even contradictory views of various orkers[9,16,17] it was thought proper to find out the ıechanism which can explain the rate maxima ccurred during hydrolysis. In the present investiıtion the hydrolysis of formamide is catalysed by ıtion exchange resin Amberlite IR-120(H). The netics of other reactions which are catalysed by sins have been studied by Nieto[19] and hers[20,21,22].

xperimental Procedure

The reaction was carried out in a vessel in which e Amberlite IR-120 resin (The Rohm and Hass ompany, Philadelphia, U. S. A.) and the formaide (B.D.H., Poole, England) solution were stirred ntinuously at constant rate using mercury seal ıss stirrer and whole apparatus was kept in a ermostatic bath to maintain constant temperature h a accuracy of ±0.1°. The reaction rate was observed by conductometer[4] (Metrohm AG, Harisav Schweiz E 382) by measuring the resistance of the solution from time to time. Resistance at zero time was calculated by extrapolating method and resistance at infinite time was noted at equilibrium (i.e., when no change in resistance was observed after sufficient time). The rate constant is calculated by the formula[23].

$$K_1 = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{R_t (R_{oo} - R_o)}{R_o (R_{oo} - R_t)}$$

where

'R_t' = Resistance at time 't'
'R_o' = Resistance at zero time
'R_{oo}' = Equilibrium resistance

Total order was determined by using the fractional life period method[23]. Entropy of activation has been calculated by using the equation[23].

$$k_r = \frac{KT}{h} e^{\Delta S/R} . e^{-E/RT}$$

Observations are as follows :

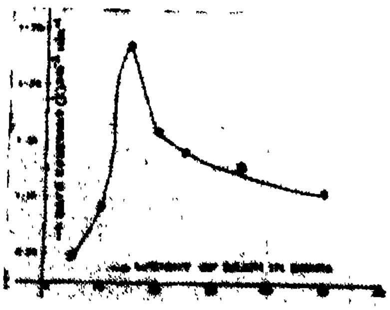


TABLE 1

EFFECT OF VARYING CONCENTRATION OF THE RESIN ON THE HYDROLYSIS OF FORMAMIDE AT 35°

Weight of Resin (gms.)	Formamide (*M*)	$k_1 \times 10^{-2}$ (min^{-1})
5	1.0	0.8998
10	1.0	1.074
15	1.0	1.644
20	1.0	1.331
25	1.0	1.261
35	1.0	1.209
50	1.0	1.125

For Correspondence : Dr. U. K. Sentiya, 557, North Civil Line, Beohar Bag, Jabalpur, M. P.
* Present address : Head, Chemistry Department, Government Engineering College, Rewa, M. P.

TABLE 2

EFFECT OF VARYING CONCENTRATION OF FORMAMIDE AT 35°

Formamide (M)	Weight of Resin (gms.)	$k_1 \times 10^{-3}$ (min^{-1})
0.5	10.0	1.127
1.0	10.0	1.074
2.0	10.0	0.9588

TABLE 3

EFFECT OF VARYING TEMPERATURE ON THE HYDROLYSIS OF FORMAMIDE

Formamide (M)	Weight of Resin (gms.)	Temperature °C	$k_1 \times 10^{-3}$ (min^{-1})
1.0	10.0	35	1.074
1.0	10.0	45	1.443
1.0	10.0	55	1.567

Results and Discussion :

The reaction has been found to be first order with respect to formamide and independent to resin concentration. Earlier workers[9,8,6,1,7,2] had also found that the reaction follows first order in acid catalysed amide hydrolysis. Different workers[1,2,10,11] have suggested different types of mechanism. Krieble and Holst[1] have suggested the reaction between formamide and the acid as the primary step

$$HC(=O)-NH_2 \rightleftharpoons HC(OH)=NH$$

$$HC(OH)=NH + H_2SO_4 \rightleftharpoons (HC(OH)=NH_2)HSO_4$$

$$(HC(OH)=NH_2)HSO_4 \rightleftharpoons HC(OH)=NH_2^+ + HSO_4^-$$

$$HC(OH)=NH_2^+ + H_2O \longrightarrow HC(=O)-OH + NH_4^+$$

Edward and Meacock[2] have suggested the reaction between amide and H^+ ion as the primary step

$$RCONH_2 \xrightarrow{H^+} RC(OH)=NH_2^+ \xrightarrow{H_2O} \text{Hydrolysis products}$$

Even if all these reactions are in evidence when an amide is added to a mineral acid it does not explain why the velocity of hydrolysis reaches a maximum and then falls off with increased acid concentration. Benrath[16] came to the conclusions that the velocity was greatest when sufficient acid was added to convert all the amide into a cation, when the acid is increased beyond this point the cation combines with the anion to form an undissociated salt which does not react with water and hence the velocity falls off. Taylor[17] comes to a somewhat similar conclusion as he says that increased acid concentration caused the formation of an unhydrolyzable complex between the acid and the amide. If this were the true explanation then the molality of the acid at maximum velocity should vary with the concentration of the amide but this does not appear to be the case.

It was observed by Duncan et al.[18] that resin when kept in water gives hydrogen ion due to the hydrolysis. This H^+ ion will reach a maximum value and then the excess of resin if added will start preventing the hydrolysis thus decreasing H^+ ions when more of resin is added consequently[11] the mechanism of reaction is

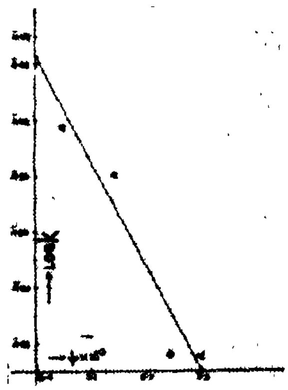
$$HCONH_2 + H^+ \xrightarrow{\text{fast}} HCONH_3^+ \xrightarrow[H_2O]{\text{slow}} HCO_2H_2^+ + NH_3$$

or

$$HC(OH)(NH_2)^+$$

According to Bender and Ginger[27] two possibilities exist for the amide, $HCONH_2$ and $HC(OH)=NH$ and two for conjugate acid of the amide $HCONH_3^+$ and $HC(OH)(NH_2)^+$. The evidence for the formation of conjugate acid of the amide was given by the work of Rietz[13] and others[12].

Values of Arrhenius parameters obtained are E(3.4 k.cals./mole) ΔS(−65.3 e.u.) and A(3.19 min^{-1}.) respectively.



The value of entropy of activation is found unusually large negative which suggests that :

1. There is decrease in the degrees of freedom in the formation of the activated complex and therefore it is a rigid one, as is also evident from the low value of frequency factor[24].

2. A small probability of the formation of the activated state because every collision with the requisite amount of energy does not necessarily lead to the formation of activated complex[25].

The value of frequency factor is also found abnormally low which suggests that :

1. Overall slowness of the reaction inspite of a rather low value of energy of activation.

2. Atomic vibrations in the activated complex are the least[24].

3. The formation of activated complex involves either separation of opposite charges or an approach of like charges[26].

An abnormally low value of frequency factor and a large negative value of entropy of activation suggests that the formation of the activated complex in reaction involves the redistribution of energy along various degrees of freedom in the reacting substrate which must be naturally a complex molecule. Hence above observation also suggest the formation of complex as the rate determining factor since hydrolysis is a slower reaction.

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Solvent Effect on Amide Hydrolysis
I—Formamide Hydrolysis in Dioxane-Water Mixtures

M. M. ELSEMONGY and H. M. ABU ELNADER

Chemistry Department, Faculty of Science, Mansoura University, Egypt

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The kinetics of formamide hydrolysis was studied in acidic and basic dioxane-water mixtures at temperatures within the range 25-60°. The variation of rate constant with temperature, dielectric constant, acidity function and solvent composition was discussed. The refined distances of closest approach for the activated complexes and the thermodynamic parameters of activation were calculated and discussed as further evidences for the solvation effects. The results were explained by the proposed mechanisms of the acid and base hydrolysis. Water ionisation constants in several dioxane-water mixtures up to 80% by weight of dioxane were also determined at eight temperatures ranging from 25 to 60° at 5° intervals. An excellent linear dependence of pK_w on the mole fraction of water in the solvent was recorded. This can be represented by an equation which facilitate the calculation of any unknown pK_w value. Plots of pK_w versus log C_w, at any temperature, give two excellent linear portions separated by a sharp boundary at a water concentration corresponding to 50 wt% of dioxane. As a surprising result, this solvent composition was coincident with the minimum in the reaction rate. The reaction rate was thus correlated with the ionisation constant of the water which is present as a component of the solvent system.

FEW investigations have been carried out on the hydrolysis of amides in aqueous-organic solvents. The propionamide hydrolysis has earlier been investigated in ethanol-water mixtures[1]. The hydrolysis of acetamide has also been studied in mixtures of water with ethanol[1], acetone[2], dioxane[3,4], methanol, glycol and glycerol[5,6], *t*-butanol[7] and isopropanol[8]. The effects of amide structure, medium and temperature on the rate constants were discussed. The mechanisms of the acid and base hydrolysis of acetamide have recently been investigated[3,4,6] in terms of the role and the effect of the solvent on the reaction rate. However, no kinetic study of the hydrolysis of formamide has been undertaken from the standpoint of solvent effects.

A new correlation between reaction rate and medium effect through water ionisation constant in aqueous-organic solvents was recently proposed[9]. The ionisation of water has been investigated in aqueous-organic solvents[10,11]. The status of measurements is not nearly so satisfactory[11]. The uncertainty in the determination of the water ionisation constant in dioxane-water mixtures[10] increases with the dioxane content of the solvent. This is caused[10] by the change in relative solubility of silver chloride and hydroxide in passing from pure aqueous solutions to those containing the higher percentages of dioxane and cannot be remedied as long as silver-silver chloride electrodes are employed[10]. Therefore, the silver-silver iodide electrode is the most convenient one for this purpose.

This investigation was planned to study the solvent effects on the kinetics and mechanism of the hydrolysis of formamide in dioxane-water mixtures. The correlation between reaction rate and medium effects was also investigated. This needs a precise measurement of the water ionisation constant for the various dioxane-water mixtures at different temperatures.

Experimental

Materials and apparatus

Pure formamide and 1,4 dioxane of "Prolabo" quality were further purified as described before[4,12]. Potential measurements were made with an Orion model 801 digital *p*H meters. Glass electrodes used with these meters were the Beckman 39004 *p*H 0-14 electrodes. The Ag, AgI electrode was prepared according to recommended procedures[13]. All the chemicals used are of the B. D. H. grade. All solutions were made up in boiled de-ionised water.

Procedure

Rates of hydrolysis were measured as mentioned before[4]. The initial concentrations of both amide and acid or base were always 0.1 *M*. The temperature was held constant within ± 0.05°. All rate constants listed are the mean of at least two completely independent determinations.

The technique of determination of water ionisation constant was that employed recently for measurements of this kind[11]. The two cells used

are represented as

glass electrode/soln A :

$HCl(C_1)$,
$KNO_3(C_2)$, in solvent S/AgI, Ag (A)

and

glass electrode/soln B :

$NaOH(C_3)$,
$NaI(C_4)$, in solvent S/AgI, Ag (B)

The advantage of this procedure is to make use of the difference in two potentials, thereby eliminating the often unknown standard potential from the calculations[11,12]. The largest source of error in the absolute magnitude of pK_w is caused by the error in determining the standard potential[10]. In all cases, the cells were maintained at the given temperature ($\pm 0.05°$) and the potential readings were recorded when they became constant to ± 0.1 mV. Measurements were repeated at least two times. Average deviations in pK_w values derived from these independent measurements were always less than 0.007 for solutions up to 50% by weight of dioxane and increased with dioxane content and reached to 0.065 for 80% by weight of dioxane.

Results and Discussion

Rate constant and energy of activation

Acid and base hydrolysis of formamide were studied in water and in dioxane-water mixtures at temperatures within the range 25-60°. The solvent composition was chosen to cover the range up to about 80.0 and 40.5% by weight of dioxane in the acid and base hydrolysis respectively. Unfortunately, dioxane has a very limited range of miscibility with aqueous sodium hydroxide which limits the significance of the results. The hydrolysis of formamide in these media is a complete reaction. The infinity values obtained were found to be constant and the same in pure water and in different dioxane-water mixtures. This assured the complete hydrolysis even in the presence of dioxane. The system was found to obey the Arrhenius equation in this wide range of temperatures. This proves that dioxane alters the reaction rate without influencing the mechanism. Second order rate constants in liter $mole^{-1}$ $second^{-1}$ were measured in the various solutions. These are collected in Table I together with the isocomposition activation energies E_c and frequency factors (log A). The rate constant decreases slightly on successive addition of dioxane in both acid and base hydrolysis, then increases passing through a minimum in case of the acid hydrolysis at about 50 wt % of dioxane. The acidity is appreciably reduced by the first additions of dioxane, passes through a minimum and finally increases again. The tetrahedral structure of water has been largely broken by successive addition of dioxane and so the proportion of free water molecules increases as the water activity decreases. In light of these effects the variation of rate constant with solvent composition can be understood. In addition, the increase in the rate constant of the acid hydrolysis at higher dioxane contents may be due to changes in ion pair formation by protonated formamide or to the breakdown of the dimer structure of formamide[14] on successive addition of dioxane, However, the effect of solvent is more pronounced on decreasing the temperature. Similar behaviour was recently observed, in this laboratory,

TABLE 1—VARIATION OF RATE CONSTANT WITH DIELECTRIC CONSTANT AND SOLVENT COMPOSITION

		I—Acid Hydrolysis							
Dioxane wt %		00.00	10.23	20 47	30.51	40.69	60.68	70.53	79.38
log C_{water}		1.745	1 699	1.623	1.590	1.517	1.338	1.200	1.066
a_{water}		1.000	0.973	0.944	0.922	0.881	0.756	0.661	0.561
$a_{dioxane}$		0.000	0.092	0.205	0.326	0.477	0.686	0.751	0.792
25°	D	78.45	69.21	60.42	51.38	42.88	25.25	17.29	11.18
	23+L	5.339	5.002	4.621	4.201	3.699	2.458	1.426	0·880
	4+log k_2	0.329	0.291	0.251	0.236	0.200	0.298	0.386	0.470
35°	D	74.89	66.01	57.49	48.84	40.16	23.89	16.36	10.60
	23+L	5.968	5.668	5.398	4.888	4.403	3.090	2.220	1.100
	4+log k_2	0.698	0.658	0.628	0.608	0.598	0.660	0.790	0.910
40°	D	73.12	64.39	55.98	47.56	39.04	23.16	15.90	10.27
	23+L	6.274	5.989	5.601	5.212	4.717	3.403	2.551	1.442
	4+log k_2	0.859	0.829	0.791	0.782	0.767	0.833	0.991	1.122
45°	D	71.44	62.91	54.56	46.34	38.11	22.58	15.47	9.99
	23+L	6.628	6.282	5.927	5.508	5.012	3.715	2.833	1.775
	4+log k_2	1.018	0.992	0.967	0.947	0.932	0.995	1.143	1.305
50°	D	69.85	61.42	52.26	45.14	36.98	21,95	15.05	9.82
	23+L	6.903	6.604	6.237	5.824	5.353	4.016	3.157	2.102
	4+log k_2	1.190	1.164	1.147	1.134	1.123	1.166	1.337	1.512
60°	D	66.62	58.49	50.48	42.58	34.69	20.68	14,25	9.21
	23+L	7.484	7.151	6.806	6.405	5.908	4.578	3.716	2.689
	4+log k_2	1.494	1.471	1.469	1.465	1.448	1.478	1.676	1.889
	E_a	15.22	15.36	15.74	15.84	15.90	16.02	16.65	18.56
	log A	7.48	7.55	7.79	7.84	7.87	8.02	8.60	10.07

		II—Base Hydrolysis					
Dioxane wt %		00.00	5.16	10.14	20.37	30.26	40.50
log C_{water}		1.745	1.722	1.699	1.648	1.591	1.529
a_{water}		1.000	0.984	0.974	0.945	0.925	0·892
$a_{dioxane}$		0.000	0.045	0.075	0.189	0.316	0.462
25°	D	78.45	73.95	69.42	60.48	51.72	42.60
	23+L	6.332	6.146	5.948	5.531	5.080	4.556
	4+log k_2	1.322	1.286	1.233	1.161	0·100	0 046
35°	D	74.89	70.52	66.21	57.55	49.00	40.34
	23+L	6.996	6.828	6.620	6.224	5.782	5.240
	4+log k_2	1.676	1.648	1.600	1.584	1.492	1.430
40°	D	73.12	68.70	64.50	56.00	47.74	39.26
	23+L	7.295	7.128	6.985	6.532	6.090	5.556
	4+log k_2	1.852	1.807	1.755	1.702	1.659	1.606
45°	D	71.44	67.15	63.00	54.64	46.56	38.20
	23+L	7.607	7.430	7.282	6.880	6.380	5.863
	4+log k_2	1.996	1.964	1.921	1.870	1.810	1.773
50°	D	69.85	65.61	61.56	53.25	45.30	37.12
	23+L	7.892	7.718	7.524	7.185	6.681	6.168
	4+log k_2	2.152	2.126	2.084	2.036	1.991	1.987
60°	D	66.62	62.41	58.49	50.54	42.82	34.81
	23+L	8.438	8.258	8.085	7·684	7.255	6.751
	4+log k_2	2.453	2.428	2.395	2.354	2.315	2.281
	E_a	14.98	14.80	15.19	15.56	15.94	16.29
	log A	7.88	8.13	8.30	8.56	8.77	8.96

during the study of hydrolysis of acetamide in dioxane-water mixtures[4].

The experimental activation energies involve a highly mixed dependence of the rate constant and of the dielectric constant of the medium on temperature[15]. In order to obtain a more precise treatment of the results the temperature dependence of the dielectric constant should be eliminated. This is achieved by calculating the isodielectric activation energies, E_d, from the corresponding rate constants in isodielectric solutions. These were obtained by interpolation, at chosen values of D, from plots of log k against D. The values of E_d were then obtained from the Arrhenius plots, and hence the contribution due to solvation phenomena will be more or less minimised. The values of E_d for the acid and base hydrolysis of formamide are listed in Table 2. The increase of both isocomposition and isodielectric energies of activation with the addition of dioxane may be due to solvation of the activated complex to a less extent than of the reactants.

Influence of dielectric constant

The increase in rate constant with increase in dielectric constant can be ascribed to the formation of an activated complex more polar than the reactants. The influence of the dielectric constant on the rate of the hydrolysis of formamide can be visualised by application of both Laidler-Landskroener equation of ion-neutral molecule interaction[1] and Amis equation of ion-dipole interaction[16]. Both equations involve a linear correlation of the logarithm of the velocity constant with reciprocal of the dielectric constant in aqueous-organic solvents. The dielectric constant, D, values of dioxane-water mixtures were obtained by interpolation from sufficiently large-scale plots of Åkerlöf's data[17]. However, the plots of log k_2 versus 1/D for the various water-dioxane compositions (Table 1) reveal that the rate decreases first linearly with decrease of the dielectric constant, then a curvature occurs specially at low dielectric constants.

The variation of velocity constant with dielectric constant can best be investigated on the basis of Elsemongy's equation[6],

$$k = k' e^{\alpha(D-1)} \quad \ldots (1)$$

where k is the velocity constant, k' is its value at D = 1, and α is a constant. This equation predicts a linear dependence of log k on D at any temperature[4,6-8]. Actually, the plots of log k_2 versus D gave very good straight lines. Following the same procedure mentioned before[6], the values of k' for the acid and base hydrolysis of formamide and the refined values of $a_{\neq}$, the distances of closest approach for the activated complexes at chosen values of D (10, 20, 40, ..., etc.), were calculated and the results are given in Table 3. The values of $a_{\neq}$ decrease with progressive addition of dioxane. This is in agreement with the fact that on progressive addition of dioxane, the structure of water would be destroyed progressively and the reacting species might become closer to each other and so the distance of closest approach should decrease[6]. However, these reasonable values account for the solvation of the activated complex and give an idea about the extent of solvation.

It is noteworthy that the radius of the activated complex in the acid or base hydrolysis of carboxylic amides of simple structure in dioxane-water mixtures seems to be almost independent of temperature and increases with increase in the dielectric constant and is, in general, dependent on the amide or the medium. This generalisation can be understood in the light of our results for acetamide[4-8] and formamide[18] in various aqueous-organic solvents.

Thermodynamic data of the activated complex

Now, it is well generally known that the role of the effect of change in solvent composition on the rate and mechanism of the reaction is conveniently expressed in terms of the thermodynamic parameters of activation, namely, the free energy change

TABLE 2—ISODIELECTRIC ENERGIES OF ACTIVATION E_d (IN K CAL/MOLE)

	I—Acid Hydrolysis					II—Base Hydrolysis				
D	10	20	40	55	75	40	50	60	70	80
E_d	18.349	16.955	16.716	16.477	16.238	17.327	17.053	16.870	16.474	15.985

TABLE 3—VALUES OF k' (IN LITER/MOLE/SEC) AND $a_{\neq}$ (IN Å)

	I—Acid Hydrolysis						II—Base Hydrolysis					
		Refined values of $a_{\neq}$ at						Refined values of $a_{\neq}$ at				
t°	4+log k'	D=10	D=20	D=40	D=60	D=80	4+log k'	D=40	D=50	D=60	D=70	D=80
25	0.601	6.2	6.5	6.6	6.7	6.8	0.719	5.8	5.9	6.0	6.1	6.2
35	1.078	6.2	6.5	6.6	6.7	6.8	1.109	5.8	5.9	6.0	6.1	6.2
40	1.314	6.2	6.5	6.6	6.7	6.8	1.327	5.8	5.9	6.0	6.1	6.2
45	1.552	6.2	6.5	6.6	6.7	6.8	1.473	5.9	6.0	6.1	6.2	6.3
50	1.724	6.2	6.5	6.6	6.7	6.8	1.648	5.9	6.0	6.1	6.2	6.3
60	2.148	6.2	6.5	6.6	6.7	6.8	2.071	5.9	6.0	6.1	6.2	6.3

TABLE 4—THERMODYNAMIC PARAMETERS OF ACTIVATION ($\Delta F^{\neq}$ AND $\Delta H^{\neq}$ IN K CAL/MOLE, $\Delta S^{\neq}$ IN E U)

		I—Acid Hydrolysis								II—Base Hydrolysis					
Dioxane wt %		00.00	10.23	20.47	30.51	40.69	60.68	70.52	79.38	00.00	5.16	10.14	20.37	30.28	40.50
25°	$\Delta F^{\neq}$	22.46	22.51	22.57	22.59	22.64	22.50	22.38	22.27	21.10	21.15	21.28	21.32	21.41	21.48
	$\Delta H^{\neq}$	14.62	14.76	15.15	15.25	15.31	15.42	16.06	17.96	13.79	14.20	14.60	14.96	15.35	15.70
	$-\Delta S^{\neq}$	26.30	25.99	24.87	24.61	24.58	23.76	21.20	14.45	24.53	23.31	22.28	21.33	20.33	19.99
35°	$\Delta F^{\neq}$	22.72	22.77	22.81	22.84	22.86	22.77	22.58	22.41	21.34	21.38	21.44	21.54	21.60	21.68
	$\Delta H^{\neq}$	14.60	14.74	15.18	15.28	15.29	15.40	16.04	17.94	13.77	14.18	14.58	14.94	15.33	15.68
	$-\Delta S^{\neq}$	26.35	26.05	24.92	24.70	24.57	23.90	21.23	14.51	24.55	23.34	22.26	21.40	20.35	19.49
40°	$\Delta F^{\neq}$	22.86	22.91	22.96	22.97	22.99	22.90	22.69	22.48	21.44	21.51	21.58	21.66	21.72	21.79
	$\Delta H^{\neq}$	14.59	14.73	15.12	15,22	15.28	15.39	16.08	17.93	13.76	14.17	14.57	14.93	15.32	15.67
	$-\Delta S^{\neq}$	26.41	26.10	25.03	24.76	24.64	23.97	21.27	14.55	24.52	23.41	22.39	21.47	20.44	19.56
45°	$\Delta F^{\neq}$	23.01	23.05	23.09	23.12	23.14	23.05	22.83	22.60	21.59	21.62	21.69	21.77	21.86	21.91
	$\Delta H^{\neq}$	14.58	14.72	15.11	15.21	15.27	15.38	16.02	17.92	13.75	14.16	14.56	14.92	15.81	15.66
	$-\Delta S^{\neq}$	26.50	26.17	25.08	24.84	24.74	24.09	21.40	14.68	24.64	23.45	22.42	21.52	20.58	19.65
50°	$\Delta F^{\neq}$	23.12	23.16	23.19	23.21	23.22	23.16	22.91	22.65	21.70	21.76	21.80	21.88	21.94	22.02
	$\Delta H^{\neq}$	14.57	14.71	15.10	15.20	15.26	15.37	16.01	17.91	13.74	14.15	14.55	14.91	15.30	15.65
	$-\Delta S^{\neq}$	26.46	26.14	25.03	24.78	24.65	24.10	21.36	14.65	24.64	23.50	22.45	21.54	20.60	19.70
60°	$\Delta F^{\neq}$	23.39	23.43	23.44	23.45	23.47	23.42	23.11	22.79	21.94	21.98	22.02	22.09	22.15	22.20
	$\Delta H^{\neq}$	14.55	14.69	15.08	15.18	15.24	15.35	15.99	17.89	13.72	14.13	14.53	14.89	15.28	15.63
	$-\Delta S^{\neq}$	26.53	26.23	25.08	24.79	24.70	24.22	21.38	14.69	24.67	23.58	22.49	21,59	20.62	19.72

$\Delta F^{\neq}$, enthalpy change $\Delta H^{\neq}$ and entropy change $\Delta S^{\neq}$. The thermodynamic properties of the activated complex are usually taken as a measure of the solvation effects. These properties have been calculated (Table 4) and are shown in Fig. 1. It is evident that solvation of one or more of the reactants will result in an increase of the activation energy and the reaction will be retarded[4,7,8]. If the solvation of the activated complex is less than that of the reactants, then the energy of activation should increase with the successive addition of dioxane. This is the case for the hydrolysis of formamide in

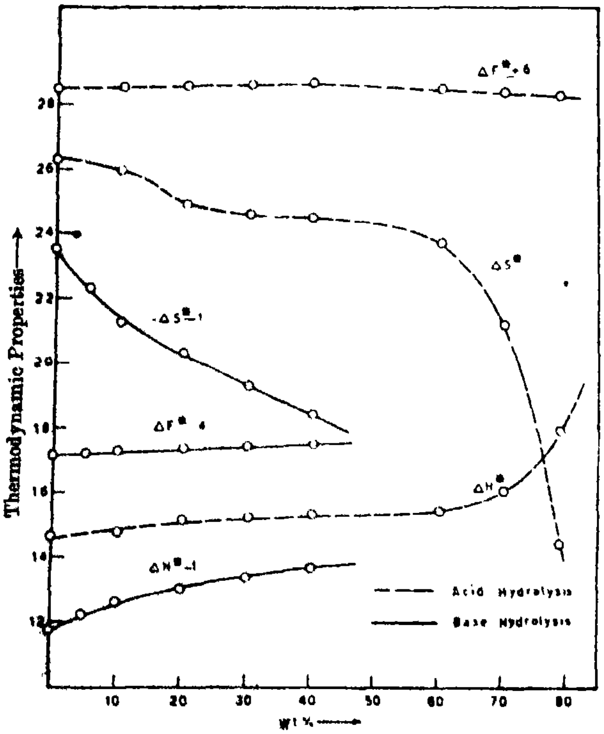


Fig. 1. Dependence of Thermodynamic properties on the composition of the solvent at 25°C.

dioxane-water mixtures. The heat content change, $\Delta H^{\neq}$, increases gradually with increasing dioxane content which may be a direct consequence of the increase of the isocomposition activation energy with decrease of dielectric constant.

It is seen that $\Delta F^{\neq}$ increases slightly with increase of dioxane concentration and then decreases also slightly by further successive addition of the organic solvent in acid hydrolysis. This weak dependence is due largely to the general linear compensation between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for a given temperature.

A major determinant of $\Delta S^{\neq}$ for reactions in solution is solvation change between reactants and transition state. The incorporation of solvent into the transition state entails a loss of entropy. $-\Delta S^{\neq}$ decreases with solvent addition in a non-linear manner. This behaviour indicates specific solvation and hence a non-random distribution of the solvent molecules. The sudden decrease of $-\Delta S^{\neq}$ noticed at about 50 wt % of dioxane in the acid hydrolysis reflects the variation of reaction kinetics with solvent composition. As mentioned above, minimum rate constants were observed at about 50 wt % of dioxane.

Water ionisation constant

To investigate the correlation between the rate of hydrolysis of formamide and medium effects[9], precise measurements of water ionisation constant were taken up.

Results of pK_w determinations in several dioxane-water mixtures (containing 10, 20, 30, 40, 50, 60, 70 and 80% by weight of dioxane) are shown in Table 5 at eight temperatures ranging from 25 to 60°. The increasing values of pK_w with increasing dioxane in the solvent system are to be expected on the basis of the decreasing dielectric constant of the medium and have been observed before[10,11] for aqueous dioxane in agreement with our results. These results are also in excellent agreement with those values at the

Table 5—Ionisation constant of water in dioxane-water mixtures

t°	Dioxane wt %									m	c
	0	10	20	30	40	50	60	70	80		
25	13.997	14.234	14.618	15.007	15.462	16.011	16.782	17.795	19.199	11.573	25.610
30	13.833	14.122	14.459	14.838	15.293	15.882	16.663	17.640	19.062	11.645	25.518
35	13.680	13.971	14.310	14.698	15.157	15.741	16.524	17.502	18.910	11.651	25.379
40	13.535	13.828	14.167	14.560	15.019	15.602	16.391	17.377	18.781	11.707	25.286
45	13.397	13.694	14.026	14.425	14.883	15.453	16.241	17.241	18.639	11.710	25.195
50	13.262	13.568	13.892	14.285	14.742	15.299	16.098	17.119	18.518	11.716	25.090
55	13.137	13.439	13.762	14.153	14.615	15.187	15.974	16.996	18.404	11.735	24.913
60	13.017	13.308	13.647	14.041	14.505	15.068	15.862	16.881	18.305	11.778	24.837

same solvent compositions obtained by interpolation of the previous data[10,11] up to about 25 wt % of dioxane. As the dioxane content increases, our pK_w values become less than the corresponding previous data[10], with differences up to 0.06 for a mixture of water with 70 wt % dioxane. The results of our pK_w determination are displayed graphically in different forms. Plots of pK_w versus mole fraction of water in the solvent X_w showed an excellent linear dependence and this can be expressed, at any temperature, by the equation

$$pK_w = c - mX_w \quad \dots (4)$$

The pK_w values of any dioxane-water mixture over the temperature range 25-60° can be computed by using equation (4). The least square values of the slopes, m, and intercepts, c, of these lines are presented in Table 5 These values facilitate the calculation of any unknown value of pK_w. Equation (4) with these numerical constants reproduces the observed values of pK_w with an average accuracy better than ± 0.008.

Plots of pK_w versus log C_w (Fig. 3) as suggested by Marshall's treatment[19] give, at any temperature, two excellent linear portions separated by a sharp boundary at a water concentration of 27.75 moles/liter (50 wt % of dioxane). Accroding to this treatment, which was intended to apply only in the case of inert cosolvents such as dioxane, the slopes of the lines provide evidence about the difference between hydration numbers of H^+ (S)+OH^- (S) and H_2O (S). However, the slope of the lines amounts to+7 in the water-rich mixtures, in excellent agreement with that obtained before[11] through the same solvent region, and reaches to +8 in the dioxane-rich mixtures. This means and proves that the internal structure of the medium suffered serious changes on addition of dioxane to water and this has recently been discussed[4].

A surprising result can be seen from the above $pK_w - \log C_w$ relation. The minimum in the reaction rate is coincident with the above mentioned water concentration of 27.75 moles/liter corresponding 50 wt % of dioxane. Above or below this water content the rate increases but the solvent effect on the kinetic behaviour is much different in these two regions. As a conclusion, the minimum of the

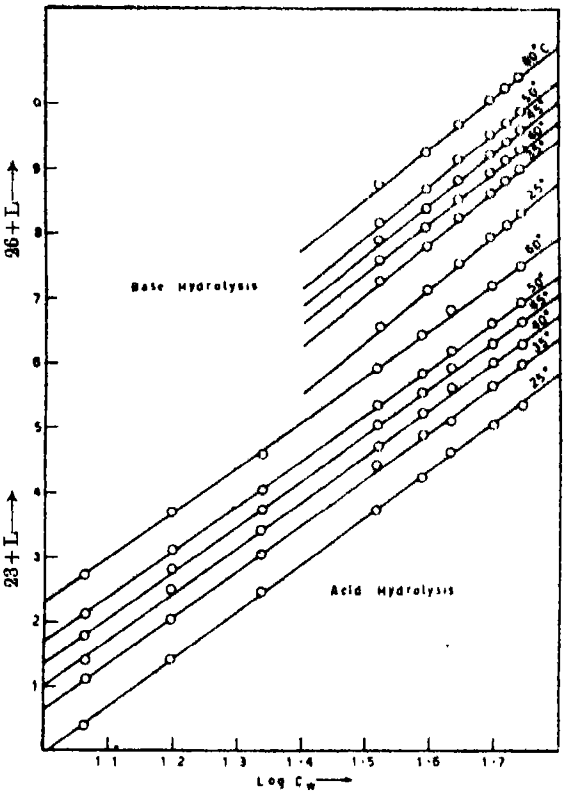


Fig. 2. Correlation of reaction rate with water ionisation constant.

reaction rate may be determined by the variation of the water ionisation constant with water concentration of the solvent system. Plots of the rate function L(L = log $k_{obs} - pK_w$) versus log C_w, at constant temperature, are very nicely linear (Table 1 and Fig. 2). Elsemongy's hypothesis[9] is therefore applicable.

$$\log k_{obs} - pK_w = n \log C_w + \text{constant} \quad \dots (5)$$

C_w is the molar concentration and K_w is the ionisation constant of the water which is present as a component of the solvent system and k_{obs} is the observed rate constant. The slope of any of these straight lines, n, constitutes a parameter which describes the manner in which the particular reaction responds to acid or base catalysis[9].

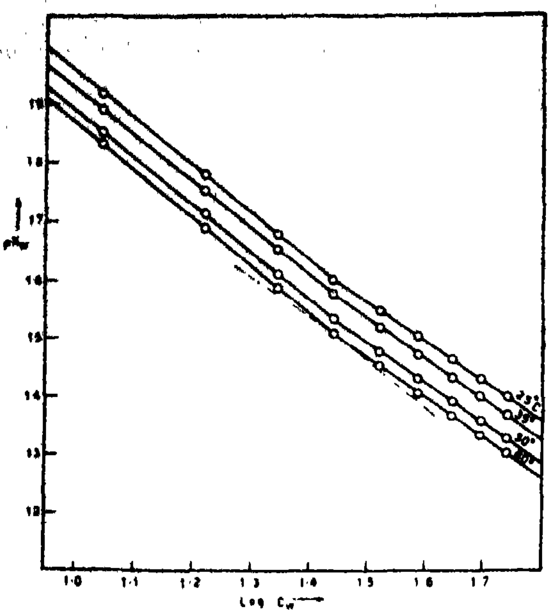


Fig. 3. Effect of water concentration on water ionisation constant in dioxane-water mixtures.

The interesting phenomenon of a rate minimum in a plot of log k_{obs} against log C_w is encountered. Such rate minima have been known for the acid hydrolysis of amides in aqueous-organic solvents[3,4,19]. Nevertheless success has been claimed in treating the phenomenon with reference to *Elsemongy's hypothesis*[9] and indeed for formamide hydrolysis the agreement is very good. This lends further strong support to the validity of the hypothesis.

In general, very good linear plots were obtained and the slopes n could be defined with certainty. These are collected in Table 6 for the acid (n_a) and

TABLE 6—VALUES OF n AT VARIOUS TEMPERATURES

t°	25	35	40	45	50	60
n_a	7.83	7.23	7.15	7.13	7.11	7.09
n_b	8.32	8.20	8.15	8.11	8.01	7.92

base (n_b) hydrolysis of formamide at the various temperatures. No great dependence of n on temperature is evident and it is clear that $n_b = n_a + 1$. This should be expected since the value of n could be looked upon as the change in number of solvated water molecules in passing from reactants to the transition state in the rate determining step[9] and the H^+ or OH^- ion, in aqueous medium, is hydrated by four or three water molecules respectively[4,6,9].

Acidity function and reaction mechanism

The results of Hammett's acidity function studies in dioxane-water[20,21] mixtures show the acidity falling to a minimum with first additions of the organic component and, then, increasing with further addition. Graphical representation of the correlation between $-H_0$ and medium composition for any fixed acid concentration in dioxa mixtures shows that the proton availa appreciably reduced by the first additions water or dioxane. Minima are exhibited a compositions (about 80 wt % dioxane HCl) depending on the fixed acid conce through the whole solvent system. T explained[21] in terms of a gradual breakd quasi-crystalline tetrahedral structure of progressive addition of dioxane. The solvation shell will be gradually dispersed proportion of non-aqueous component is i and the aqueous solvates (n H_2O, H^+) will b ed by H_3O^+ ions at the minima of the plots $-H_0$ to medium composition. Reaching the the increase in $-H_0$ with further addition organic solvent was supposed to result fr replacement of the H_3O^+ ions by the SH^+ io

Application of Zucher-Hammett or treatments[20] showed that the kinetic beha not parallel to the changes in acidity functi with change in solvent composition. Our tions have shown that the rates of hydr formamide in dioxane-water mixtures consistent with any of these previous tr which correlate rates with acidity function may be due to the fact that the concept of th function loses some of its generality on passi aqueous solutions to media of lowest c constants[9]. The observed deviations, in t hydrolysis, are probably due to the fact t maximum in H_0 is not coincident with the m in the reaction rate. The bimolecular rate follows a trend which is far from linear in the operation of our proposed bimolecular a mechanism.

All previous results reveal that the proposed mechanisms for the acid[4] and hydrolysis of acetamide in dioxane-water n are the operating mechanisms. Thus i hydrolysis a mechanism involving a rapid p tion pre-equilibrium on either the oxygen or n atom by solvated protons followed by bimolecular addition of water to the s protonated amide may be propose equilibrium was established between O- and N nated transition states. The positive charge distributed over the oxygen and nitrogen at the amide in the initial state is further distributed to the other oxygen atoms arise the solvating water molecules on wa mixtures. The changes in polarity are the and only a small solvent effect would be e in agreement with our observations in these In the dioxane-rich region, the transition probably involved in a proton transfer rea which the proton is transferred from the atom to the nitrogen atom. The reaction nitrogen-protonated formamide and wa accompanied by an increase in polarity a transition state then decomposes to the proc a relatively high rate which is in agreement w

observed relatively high rates in dioxane-rich regions. In base hydrolysis, a fast pre-equilibrium nucleophilic attack of solvated hydroxyl ions on the amide molecule proceeds the slow bimolecular addition of a water molecule to the solvated transition state.

Energies and entropies of activation together with the frequency factors (log A) given in Tables 1 and 4 are further evidences supporting the validity of our proposed bimolecular mechanisms.

Solvent composition and reaction rate

An explanation for the decrease of the reaction rate would be that a water molecule bound by a hydrogen bond to a dioxane molecule is less nucleophilic than a water molecule bound by a hydrogen bond to another water molecule. The variation of the reaction rate with water concentration is illustrated by a plot of log k_2 against log C_w. In acid hydrolysis, two linear portions were obtained corresponding to water- and dioxane-rich solvent mixtures. Their slopes vary with temperature and have the values 0·6-0.4 and 0.7-1.4 at 25-60° respectively. In base hydrolysis, straight lines were obtained and their slopes vary also with temperature and have the values 1.2-0.9 at 25-60°. These slopes, as generally known, represent the number of water molecules involved in the formation of the activated complex. The rate is thus proportional to the concentration of water, in agreement with the expected bimolecular mechanisms.

The variation in reaction rate with solvent composition, at constant acid or base concentration, may be ascribed primarily to changes in the solvent system through the equilibrium,

$$(H_2O)_3I + n\,S \rightleftharpoons n\,H_2O + (H_2O)_{3-n}S_nI \quad \ldots \quad (6)$$

where I stands for a H_3O^+ or OH^- ion. This can be considered in the light of the assumption of a multi-step solvation mechanism[28]. A H_3O^+ or OH^- ion, that is hydrated by three water molecules in pure aqueous solvents, can be expected to exist as such clusters as $(H_2O)_{3-n}S_nI$ in mixed solvents[4,6,9,20,23]. However, the net reaction actually taking place is the substitution of water by dioxane in the cluster. Therefore the number of free water molecules increases on progressive addition of dioxane and this plays an important role in the dependence of reaction rate on solvent composition. In addition, this may explain the increase of acidity, at high dioxane content in dioxane-water mixtures, at a fixed acid concentration, through the formation of the more acidic non-solvated H_3O^+ ions. Thus, the decrease in $-H_0$ with addition of dioxane may also attributed to the shift of equilibrium (6) to the right. The protonated species were supposed changing from $(H_2O)_4\,H^+$ to water solvated SH^+ ions. At the minimum of $-H_0$, the protonated species changes from water solvated SH^+ ions to H_3O^+, and only at very high concentrations of dioxane they change to dioxane solvated SH^+ ions resulting in the increase of $-H_0$.

Presumably, the water solvated SH^+ ion exists [$S(H_2O)_3$] H^+, or possibly SH^+ $(H_2O)_n$, with species solvated by iceberg-like structure of wat The equilibrium constant is given, in terms activities, by the equation

$$K = \frac{(a_{H_2O})^n\, a_{solv \cdot I}}{(a_S)^n\, a_{hyd \cdot I}}$$

Thus the ratio $(a_{hyd \cdot I}/a_{solv \cdot I})$ is directly p portional to $(a_{H_2O}/a_S)^n$ and the reaction rate wo be dependent on each of these two terms. This be proved by plotting log k_2 against log $(a_{H_2O}/$ where very good straight lines were obtain (Fig. 4). Activities of water and dioxane w

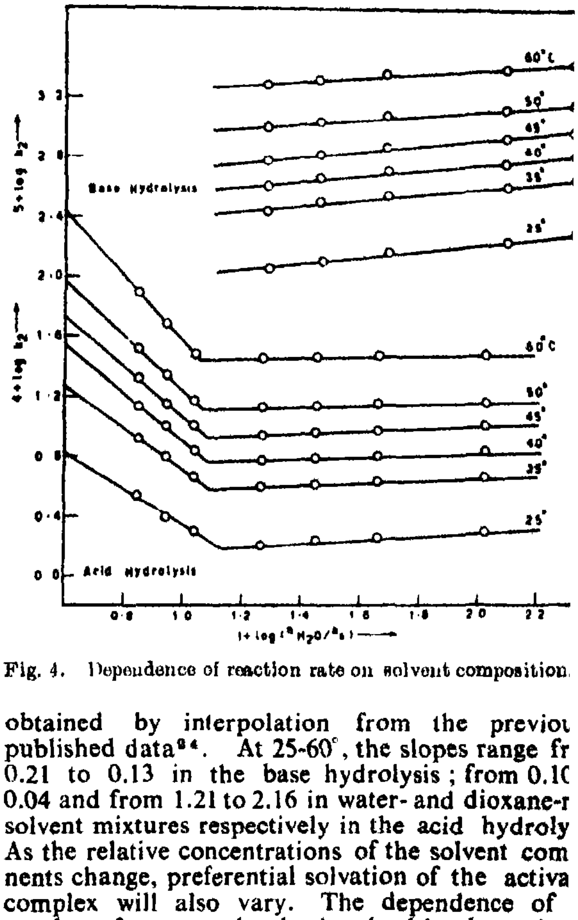


Fig. 4. Dependence of reaction rate on solvent composition.

obtained by interpolation from the previou published data[24]. At 25-60°, the slopes range fr 0.21 to 0.13 in the base hydrolysis ; from 0.1 0.04 and from 1.21 to 2.16 in water- and dioxane-r solvent mixtures respectively in the acid hydroly As the relative concentrations of the solvent com nents change, preferential solvation of the activa complex will also vary. The dependence of number of water molecules involved in the activa complex on solvent composition is again a str evidence of the continuous substitution of water dioxane molecules as dioxane is increased.

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Dielectric Properties of Amides : Molar Polarization, Relaxation Time and Dipole Moment of Amides in Benzene and Dioxane Solutions

P. P. RASTOGI

Department of Chemistry, Lucknow University, Lucknow, India

and

P. C. TEWARI and B. P. PRADHAN

Department of Physics, Lucknow University, Lucknow, India

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Molar polarization, relaxation time and dipole moment of five amides like Formamide, N-methylacetamide (NMA), N : N-dimethylformamide (DMF), N : N-dimethylacetamide (DMA) and Acetamide have been determined in benzene and dioxane solutions at 25° using the standing wave technique of Roberts and Von Hippel[1] in 3 cm region. The reported results on dipole moment have inferred the existence of a 'trimer' for formamide and a 'dimer' for NMA in benzene as compared to 'monomers' of these amides in dioxane solutions.

A number of communications have appeared[2-6] reporting the dielectric properties of amides to examine the mode of interaction and the role of self-association or intermolecular hydrogen bonding in view of their bio-medical and industrial utility as well as much similarity with water. Although, the subject has received considerable attention through Raman and Infra-red recordings ; but still the findings are limited and scanty in view of the complications involved in solution measurements. Moreover, the data for formamide and DMF have been found to be less conclusive[7]. Thus, from this point of view the present studies are undertaken to illustrate and establish the state of amides as well as to describe their behaviour in solutions from dipole moment measurements.

Experimental

The microwave bench of 3 cm (Type KLB-019 No. 0671, made in India) has been employed for the determination of dielectric constant, ϵ_1, and dielectric loss, ϵ_2, by the standing wave technique of Roberts and Von Hippel[1], using the simplified relations of Dakin and Works[9] as described earlier[10,11]. These ϵ_1 and ϵ_2 values have been used to calculate the relaxation time, τ, and dipole moment, μ, by Gopal Krishna[12] fixed frequency method for dilute solutions, using the following equations :

$$X=\frac{\epsilon_1(\epsilon_1+1)+\epsilon_2^2-2}{(\epsilon_1+2)^2+\epsilon_2^2} \quad \dots (1)$$

$$Y=\frac{3\epsilon_2}{(\epsilon_1+2)^2+\epsilon_2^2} \quad \dots (2)$$

$$\tau=\frac{\lambda}{2\pi C}\left(\frac{dY}{dX}\right) \quad \dots (3)$$

$$\mu^2=\frac{9\,kT}{4\pi N}\,\frac{M}{d}\left\{1+\left(\frac{dY}{dX}\right)^2\right\}\left(\frac{dX}{dW}\right) \quad \dots (4)$$

where λ, C, k, N and T represent their usual meaning, d the density of solvent and M and W are the molecular weight and weight fraction of solute respectively.

In order to make an estimate of the precision of equipment, the dipole moments of some of the liquids like, methanol, pyridine and acetone are determined in benzene solution and are given in Table 1 along with their reported values for the sake of comparison. The experimental and literature values are found to be wiihin the maximum deviation of −3%. The obtained lower values of μ are expected to be probably due to the solvent effect[13,14].

TABLE 1

Dipole moment (μ) of methanol, pyridine and acetone in benzene solution at 25°

Substance	$\mu\times10^{18}$ e. s. u. Experimental	Literature[a]
Methanol	1.63	1.68
Pyridine	2.14	2.20
Acetone	2.68	2.76[b]

a. G. C. Pimental and A. L. McClellan, "The Hydrogen Bond" Reinhold Publishing Co., New York, N. Y. (1960), p. 15.

b. C. P. Smyth, "Dielectric Behaviour and Structure" McGraw Hill Book Co., New York (1955), p. 48.

Formamide and N : N-dimethylformamide supplied by B.D.H. India were treated with freshly ignited quicklime, kept overnight, distilled under reduced pressure and the middle fraction of the distillate collected. The process of purification repeated until the specific conductance of the dis-

tillate reduced to about 10^{-6} ohm^{-1} cm^{-1} at 30°. Whereas N-methylacetamide, N : N-dimethylacetamide and acetamide obtained from E. Merck, Germany ; and dioxane and benzene Analar Grade purchased from B. D. H., India were used without further treatment.

Results

The dielectric constant, ϵ_1, dielectric loss, ϵ_2, and molar polarizability, P, of formamide, NMA, DMF, DMA and acetamide in benzene and dioxane solutions at different concentrations at 25° are recorded in Tables 2 and 3 respectively. The slopes (dy/dx) and (dx/dw) evaluated from the linear plots of x, y and x, w respectively are used to calculate dipole-moment, μ, and relaxation time, τ, by Gopal Krishna fixed frequency method[1,2]. The determined values of (dy/dx), (dx/dw), τ and μ are summarised in Table 4.

TABLE 2

Dielectric Constant (ϵ_1), Dielectric Loss (ϵ_2) and Molar Polarizability (P) of amides in Benzene at different concentrations and at 25° (λ = 8.28 cm.)

Weight fraction (W)	ϵ_1	ϵ_2''	$P=\left(\frac{\epsilon_1-1}{\epsilon_2+2}\right)\frac{M}{d}$ cm³
	Formamide		
0.0208	2.29	0.027	15.0
0.0389	2.85	0.046	15.8
0.0561	2.42	0.059	16.1
0.0746	2.46	0.081	16.7
	N-Methylacetamide		
0.0162	2.57	0.161	22.2
0.0318	2.62	0.239	29.3
0.0480	2.66	0.298	29.5
0.0622	2.70	0.349	29.9
	N : N-Dimethylformamide		
0.0251	2.68	0.166	29.8
0.0381	2.75	0.306	30.6
0.0595	2.94	0.545	32.5
0.0748	3.00	0.735	34.2
	N : N-Dimethylacetamide		
0.0084	2.42	0.068	31.7
0.0196	2.63	0.144	34.8
0.0282	2.70	0.206	35.7
0.0323	2.78	0.223	36.8

TABLE 3

Dielectric Constant (ϵ_1), Dielectric Loss (ϵ_2) and Molar Polarizability(P) of amides in Dioxane at different concentrations and at 25° (λ = 3.23 cm.)

Weight fraction W	ϵ_1	ϵ_2	$P=\left(\frac{\epsilon_1-1}{\epsilon_2+2}\right)\frac{M}{d}$ cm³
	Formamide		
0.0075	2.66	0.216	15.5
0.0103	2.69	0.302	15.7
0.0207	2.74	0.528	16.0
0.0314	2.77	0.676	16.2
	N-Methylacetamide		
0.0052	2.66	0.243	25.2
0.0096	2.68	0.286	25.4
0.0129	2.69	0.320	25.6
0.0168	2.77	0.406	26.2
	N : N-Dimethylformamide		
0.0045	2.59	0.224	24.6
0.0088	2.66	0.270	25.2
0.0153	2.74	0.369	26.0
0.0306	2.88	0.455	27.3
	N : N-Dimethylacetamide		
0.0110	2.58	0.200	28.4
0.0202	2.68	0.261	30.3
0.0252	2.75	0.307	31.0
0.0375	2.88	0.424	32.6
	Acetamide		
0.0060	2.60	0.167	19.9
0.0101	2.64	0.217	20.2
0.0155	2.74	0.290	20.9
0.0312	2.90	0.448	22.1

TABLE 4

(dy/dx), (dx/dw), τ and μ values of Formamide, NMA, DMF, DMA and Acetamide in Benzene and Dioxane solutions at 25°

Amides	(dy/dx)	(dx/dw)	$\tau\times10^{12}$ sec.	μ Debye
		Benzene		
Formamide	0.24	0.45	4.1	1.11
NMA	1.19	0.41	20.4	2.03
DMF	1.09	1.15	18.7	3.24
DMA	0.37	2.43	6.3	3.03
Acetamide	—	Insoluble	—	—
		Dioxane		
Formamide	2.30	1.03	39.4	3.69
NMA	1.64	0.80	28.0	3.17
DMF	0.58	2.50	9.9	3.39
DMA	0.54	2.38	9.2	3.55
Acetamide	0.74	1.70	8.0	2.73

Discussion

It is interesting to observe from Table 4 that the dipole moment of all amides are considerably higher in dioxane to those obtained in benzene solutions. For the hydrogen bonded solvents like, formamide and N-methylacetamide ; the μ values 1.11 D and 2.03 D in benzene as compared to 3.69 D and 3.17 D in dioxane are strikingly small i.e., almost 1/3rd for formamide and 2/3rd for NMA concluding the existence of 'trimer' for formamide and 'dimer' (or

better 'dimer equilibrium') for NMA in benzene[4] to that of 'monomers' in dioxane solutions. This observed anomaly can be reasonably explained in terms of the much stronger dioxane-amide interaction as compared to intermolecular hydrogen bonding in amides : indicating the existence of free molecular dipoles or 'monomers' in dioxane solutions. However, this peculiarity was found to be missing in non-hydrogen bonded solvents like, DMF and DMA on account of the absence of amino hydrogen for bonding to oxygen of neighbouring molecules. The remarkably large decrease for formamide suggests the association at both of the amino hydrogens and the moderate deviation for NMA indicate the intermolecular bonding at amino hydrogen such that the adjacent molecular dipoles are not parallel, but inclined in opposing direction to one another thereby resulting in a net lower dipole moment for trimer and dimer in benzene than for monomers in dioxane in contradiction to the statement advanced by Meighan and Cole[7,8]. An 'Extended' H bridge model for NMA 'dimer' in benzene has been proposed [supported by spectroscopic evidence[15] as shown in Fig. 1], on the basis of the calculated[14] angle of inclination (142° 40'), using the 'monomers' dipole moment determined in dioxane solution.

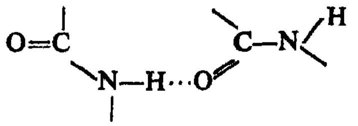


Fig. 1. Model of NMA 'dimer' in benzene

Finally, the existence of a 'trimer' for formamide and a 'dimer' for NMA in benzene has been inferred as compared to 'monomers' for all amides in dioxane solutions.

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An Attempt to Account Quantitatively for the Electroviscous Behaviour of Some Colloidal Ampholytes

B. N. GHOSH

University College of Science & Technology, Calcutta-700 009.

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For Colloidal ampholytes, Smoluchowski's electroviscosity equation has been modified by taking into consideration the contribution of the ampholyte molecules to the specific conductivity of the solution.

EQUATIONS, to suit special cases such as (1) the variation of η_{sp}/C with C, the concentration of the ampholyte when the pH and ionic strength of the system are kept constant and (2) the variation of η_{sp}/C with S, the concentration of an added strong electrolyte at constant C and pH, have been deduced starting from this modified equation. These equations have been found to agree satisfactorily with the data available in the literature on viscosity measurements of the globular proteins, bovine serum albumin, ribonuclease and β-lactoglobulin at pH corresponding to their isoionic points and also at other values of pH. It follows from the equation on the variation of η_{sp}/C with C that at $Lt_{c}\rightarrow O$, the excess of intrinsic viscosity over $Kv/100=0.0188$, (where $K=2.5$ and $v=0.75$, the specific volume of the protein) is a part of the electroviscous effect and that part is independent of C. In the literature, this excess of intrinsic viscosity has so long been attributed to the hydration of the protein molecules.

In the electroviscous equations of Smoluchowski[1] and Booth[2] it has been assumed that the colloidal particles act as non-conductors. Briggs[3] has expressed doubt on the validity of this assumption with reference to colloidal electrolytes. In a previous publication the author[4] has pointed out the necessity of taking into consideration the contribution of the colloidal particles to the specific conductivity term in the electroviscosity equation of Smoluchowski.

The Smoluchowski equation may be written as follows :—

$$\eta_{sp}=K\frac{Cv}{100}\left[1+\frac{1}{\eta a^2\lambda}\left(\frac{D\zeta}{2\pi}\right)^2\right] \quad \ldots \quad \ldots \quad (1)$$

where η_{sp} denotes the specific viscosity of the solution, K is a constant and according to Einstein it is equal to 2.5 for spherical particles, C, the concentration of the colloid in gram per 100 ml of the solution, v, the specific volume of the colloid, 'a', the radius of the particles, ζ, their electrokinetic potential and D, η and λ are the dielectric constant, viscosity and specific conductivity respectively of the dispersion medium.

It has been shown by the author in previous publications[5-7] that λ the specific conductivity of the solution of a colloidal electrolyte is made up of two parts, one part $\theta\lambda_s$ contributed by the colloidal particles and the other part $(1-\theta)\lambda_i$ contributed by the intermicellar solution (i.e., the dispersion medium) and they are related by the equation ;

$$\lambda=\theta\lambda_s+(1-\theta)\lambda_i \quad \ldots \quad \ldots \quad (2)$$

where λ_s is constant for a well-dialysed pure sol and represents the specific conductivity of the double layer at the plane of contact with an electrode of the conductivity cell, θ, the fraction of the surface per unit area of an electrode covered by the diffuse double layers of the particles and θ is equal to $C/(K_o+C)$ where K_o is a constant and C the concentration (unit arbitrary) of the colloidal particles.

Derivation of the equations :

Substituting the values of λ and θ in equation (1) and putting $A=\frac{1}{\eta a^2}\left(\frac{D}{2\pi}\right)^2$ we get the following equation :

$$\eta_{sp}/C=K\frac{v}{100}\left[1+\frac{A\zeta^2(C+K_o)}{\lambda_s(C+K_o\lambda_i/\lambda_s)}\right] \quad \ldots \quad \ldots \quad (3)$$

In a sol, highly purified by dialysis, λ_i is much smaller than λ_s and if the solution is diluted with water then it follows from equation (3) that η_{sp}/C will increase as C decreases, since all the other terms remain constant.

If a strong electrolyte, in small quantity, is added to the solution then ζ and λ_s diminish slightly but λ_i increases sharply. As the concentration of the added electrolyte is increased gradually λ_i increases more and more and when the level of concentration reached is such that C in the denominator of equation (3) becomes negligible compared to $K_o\lambda_i/\lambda_s$ theu equation (3) assumes the form

$$\eta_{sp}/C=K\frac{v}{100}\left[1+\frac{A\zeta^2}{\lambda_i}+\frac{A\zeta^2}{K_o\lambda_i}C\right] \quad \ldots \quad \ldots \quad (4)$$

$$=K\frac{v}{100}\left[1+A_1+\beta C\right] \quad \ldots \quad \ldots \quad (5)$$

where $A_1=A\zeta^2/\lambda_i$ and $\beta=A\zeta^2/K_o\lambda_i$

If the concentration of the added electrolyte is now fixed and only C is increased then η_{sp}/C will increase linearly with C, since all the other terms in equation (5) remain constant. It is to be noted that since the constants A_1 and β are determined from viscosity data they may include a proportionality constant.

Variation of η_{sp}/C with electrolyte concentration at constant C :

Let $(\eta_{sp}/C)_o$ and $(\eta_{sp}/C)_s$ denote respectively the values of η_{sp}/C when the concentration of the added electrolyte is zero and S respectively and let their ratio $(\eta_{sp}/C)_s : (\eta_{sp}/C)_o$ be denoted by R. Then an equation connecting the variation of R with S over a limited range of the latter, may be deduced from equation (3) in the following way :

*Let ζ change to $\zeta(1-aS)$ and λ_i change to $\lambda_i(1+hS)$ as the concentration of the added electrolyte changes from zero to S. Now putting $A_o = A(C+K_o)$ in equation (3) we may write as follows :

$$R = K\frac{v}{100}\left[1+\frac{A_o\zeta^2(1-aS)^2}{C\lambda_s+K_o\lambda_i(1+hS)}\right] : K\frac{v}{100}\left[1+\frac{A_o\zeta^2}{C\lambda_s+K_o\lambda_i}\right]$$

$$= \left[\frac{B+(K_o\lambda_i h-2A_o a\zeta^2)S}{(H+K_o\lambda_i hS)}\times\frac{H}{B}\right]$$

$$= \left[1-\frac{mS}{m_o+S}\right] \qquad (6)$$

where terms in $(S)^2$ have been neglected and $B = (C\lambda_s+K_o\lambda_i+A_o\zeta^2)$.

$$H = (C\lambda_s+K_o\lambda_i),$$

$$m = \left[\frac{(K_o\lambda_i h/H)-(K_o\lambda_i h-2A_o a\zeta^2)/B}{(K_o\lambda_i h)/H}\right]$$

and $m_o = H/K_o\lambda_i h$

In equation (6) m and m_o are constants, since all the terms contained in them remain constant when S alone is varied.

Isoionic point and the application of the equations :

The application of the equations mentioned above to proteins at their isoionic point may be questioned since at this point their not charge is zero or nearly so. It may be pointed out in this connection that since the charged sites on a protein molecule are separated by a distance[8,9], each of them will have its own ion atmosphere and there will be a difference, of potential. say ζ, between the charged site and its ion atmosphere in the solution.

The average of ζ will be zero but the average of ζ^2 will always have a positive value†. Therefore, theoretically there can be no objection against the use of the aforesaid equations on any protein even at its isoionic point.

Source of data and observation of the investigators

Tanford and Buzzell[9] have investigated the viscous properties of bovine serum albumin (BSA) solutions at different values of pH and ionic strength. Crystalline bovine serum albumin, obtained from Armour and Co, is dissolved in water and the solutions are deionised and brought to isoionic pH by passing them through ion-exchange column as described by Dintzis[10]. The pH of a solution is adjusted by adding appropriate amounts of HCl or KOH and its ionic strength is fixed by adding the required amounts of KCl. The ionic strength has been defined as the total concentration of an electrolyte (all univalent) and according to them it is a compromise between two extreme procedures, "that of counting a protein molecule with a net charge of Z, as a Z valent ion, which because of the wide separation of charges, is clearly inappropriate and that of not counting the protein charges at all."

The viscosity and density of the solutions have been measured at 25° with proper care. They have observed that at constant pH and ionic strength η_{sp}/C varies linearly with C and that the intrinsic viscosity $[\eta]$ found by extrapolating the line to $C=0$, at the isoionic point, is practically constant, $[\eta]=0.0369\pm0.0010$ for all ionic strengths except $\mu=0$, but at $\mu=0$, $[\eta]$ 0.0406. It has also been observed that at ionic strength above 0.01 change of pH between 4.3 and 7.3 affects $[\eta]$ only slightly. Its average value in these ranges of pH and ionic strength is 0.0371 ± 0.0009.

The aforesaid authors[11] have also investigated at 25° the viscous properties of ribonuclease over a wide range of pH and ionic strength. Crystalline ribonuclease of bovine origin obtained from Armour & Co. is dissolved in water and the solutions are deionised and brought to isoionic point by passing them through ion-exchange column. Their pH and ionic strength are adjusted at the desired levels in the same way as in the case of BSA. They have found that at constant pH and ionic strength η_{sp}/C varies linearly with C and that no significant change in $[\eta]$ occurs between pH 5.9 and pH 11 at ionic strength above 0.01. The mean value of $[\eta]$ in these ranges of pH and ionic strength, with its root mean square deviation is 0.033 ± 0.0004. Their data are recorded in the Tables 1, 2, 5 and 6 of this paper.

The electroviscous properties of β-lactoglobulin have been investigated by Briggs and Hanig[12] at 25°. Crystalline β-lactoglobulin prepared by a modification of Palmer's method has been recrystallised twice, Since this protein crystallises at its isoelectric point (pH 5.18) after prolonged dialysis against distilled water no further purification has been considered necessary for the preparation of isoionic solution.

* Slight variation in λ_s is completely overshadowed by the variation in λ_i and so the former can be neglected. The linear variation of ζ and λ_i with S, assumed above, is expected to hold good as S is small.

† Similar views have also been expressed by previous authors. [8,9]

On the acid side of the isoionic point, pH of the solutions has been adjusted by adding HCl, and on the alkaline side by adding NaOH. The salt content of the solutions has been adjusted by adding the required amount of NaCl.

Their data taken from the Tables 2a, 2b and 2c of their paper are recorded in the Tables 3, 4, 7 and 8 of this paper.

Notes on data recorded in the tables.

In Table 1 are recorded the data on measurement of viscosity of bovine serum albumin (BSA) at 25° at the isoionic point (pH about 5.0) and also at pH 8.5 by Tanford and Buzzell[9]. These data are taken from Table 1 and Figure 1 of their paper.

In column 2 of Table 1, C represents the concentration in grams of BSA per 100 ml. of the solution. The other terms have the same significance as discussed already.

TABLE 1

INCREASE OF η_{sp}/C WITH THE CONCENTRATION C OF BSA

Miscellaneous	C	Values of η_{sp}/C Observed	Calculated
Isoionic	0	0.0369	0.0368
pH nearly 5.0	0.60	0.0395	0.0393
Ionic strength-0.002	1.30	0.0423	0.0421
Equation used (5)	1.70	0.0438	0.0437
K=2.5	2.53	0.0176	0.0470
V/100=0.0075	3.37	0.0510	0.0504
A_1=0.96	4.22	0.0542	0.0538
β=0.213			
pH 8.5	0	0.0406	0.0406
Ionic strength—0.02	1.10	0.0475	0.0466
Equation used (5)	1.64	0.0512	0.0515
	2.70	0.0579	0.0579
K=2.5	3.43	0.0625	0.0626
V/100=0.0075	4.07	0.0672	0.0667
A_1=1.16			
β=0.34			

In Table 2 are recorded the data of Buzzel and Tanford[11] on measurements of viscosity of ribonuclease at 25°, at the isoionic point (pH 9.6) and also at pH 5.9. These data are selected from Table 1 and Figure 1 of their paper. There is a printing error in Figure 1 of their paper in which 4.5 should be read instead of 5.0, on the ordinate. The terms used in Table 2 have the same significance as in Table 1.

In Table 3 of this paper are recorded the data of Briggs and Hanig[13] on measurements of viscosity of β-lactoglobulin at the isoionic point (pH 5.20 approximately) in the presence of 0.05 moles of NaCl per liter. These data have been collected from Table 2c of their paper. Table 4 contains the data of the same authors taken from Table 2a of their paper. In Table 4, m represents the electrophoretic velocity of the protein molecules under unit potential gradient.

TABLE 2

INCREASE OF η_{sp}/C WITH C OF RIBONUCLEASE

Miscellaneous	C	Values of η_{sp}/C Observed	Calculated
Isoionic point	0	0.0927	0.0927
Ionic strength-0.05	1.45	0.0968	0.0969
Equation used (5)	2.07	0.0378	0.0379
K=2.5	2.48	0.0384	0.0398
V/100=0.0075	3.50	0.0416	0.0415
A_1=0.74	4.14	0.0426	0.0430
β=0.133			
pH 5.9	0	0.0382	0.0338
Ionic strength-0.02	0.97	0.0360	0.0363
Equation used (5)	1.56	0.0382	0.0382
K=2.5	2.34	0.0408	0.0407
V/100=0.0075	3.28	0.0434	0.0437
A_1=0.77	4.11	0.0461	0.0464
β=0.17			

The other terms in the Tables 3 and 4 have the same significance as stated already.

TABLE 3

DATA ON η_{sp}/C OF β-LACTOGLOBULIN FOR DIFFERENT VALUES OF C

Miscellaneous	C	η_{sp}	Values of η_{sp}/C Observed	Calculated
Isoionic point	0			0.0378
NaCl—0.05N	0.5	0.0196	0.0392	0.0378
Equation used (3)				
K=2.5	1.0	0.0367	0.0367	0.0378
V/100=0.0075				
A_1=1.01	2.0	0.0745	0.0373	0.0378
$\lambda_s=\lambda_1$				

TABLE 4

VARIATION OF η_{sp}/C WITH C OF β-LACTOGLOBULIN AT pH 4.22±0.05

Miscellaneous	C	$m\times10^4$	η_{sp}	Values of η_{sp}/C Observed	Calculated
NaCl—Nil	0				0.0577
Equation used	0.5	2.12	0.0256	0.0512	0.0521
$\eta_{sp}/C=\left[1+\frac{6.2}{C+3}\right](0.0188)$	1.0	1.75	0.0468	0.0468	0.0479
	2.0	1.41	0.0886	0.0443	0.0421

In the Tables 5 and 6 of this paper are recorded the data on the variation of R of BSA and ribonuclease with S at constant protein concentration C. S represents the ionic strength or the total concentration of the added electrolyt and since the solutions of the proteins are at their respective isoionic points no addition of acid or alkali is required to adjust the pH. Therefore, the total concentration is the concentration of KCl required to adjust the ionic strength of the solutions and it is the same as S in equation (6). $[\eta]$ in these tables represents the intrinsic viscosity. In Table 6 the mean values of $[\eta]$ have been recorded excepting the first one.

TABLE 5

VARIATION OF R WITH S, BSA CONCENTRATION—8g. PER 100 ml.

Miscellaneous	S	$[\eta]$	η_{sp}/C	Values of R Observed	Values of R Calculated
*Isoionic point pH=5.0 nearly	0	0.0406	0.0568	1.0	1.0
C=8 per cent	0.001	0.0362	0.0512	0.902	0.908
Equation used (6)	0.002	0.0369	0.0469	0.861	0.869
	0.010	0.0361	0.0466	0.820	0.820
m=0.199					
m_0=0.00108	0.085	0.0382	0.0457	0.801	0.804

* According to the authors* pH increases from 5.0 to about 5.6 as S changes from 0 to 0.15.

TABLE 6

VARIATION OF R WITH S, RIBONUCLEASE—8g. PER 100 ml.

Miscellaneous	S	$[\eta]$	η_{sp}/C	Variation of R Observed	Variation of R Calculated
Isoionic point pH 9.6	0	0.0336	0.0447	1.0	1.0
C=8 per cent	0.001	0.033	0.0432	0.966	0.966
Equation used (6)	0.01	0.038	0.0411	0.919	0.919
m=0.096	0.02	0.033	0.0408	0.918	0.912
m_0=0.00181	0.05	0.033	0.0405	0.906	0.907

In the Tables 7 and 8 are recorded the data of measurements of Briggs and Hanig[11] on viscosity of β-lactoglobulin at different concentrations S of NaCl, the *p*H and the protein concentration C of the solutions being maintained constant at the desired levels.

Discussions

For the globular proteins mentioned in this paper K=2.5 and their specific volume† V=0.75, so in equation (1) Kv/100=0.0188. The data recorded in the Tables 1 and 2 show that η_{sp}/C of BSA and ribonuclease increase with the increase of C and the agreement between the values of η_{sp}/C observed and those calculated by using equation (5) is quite satisfactory at values of *p*H corresponding to the isoionic points and also at other values of *p*H. It is to be noted that at C→O the excess of intrinsic viscosity over 0.0183 is given by the expression $0.0188A_1=0.0188\left[\frac{\zeta^2}{\eta a^2\lambda_1}\left(\frac{D}{2\pi}\right)^2\right]$ which is a part of the electroviscous effect independent of C. In the literature this is usually attributed to the hydration of the protein molecules. Equation (5) thus leads to the conclusion that in the case of the globular proteins the intrinsic viscosity in excess of 0.0188, so long attributed to hydration, is but a part of the electroviscous effect.

The data on β-lactoglobulin, at the isoionic point in the presence of 0.05 N NaCl, recorded in Table 3 show that η_{sp}/C remains practically constant when C is varied. The data fit the equation $\eta_{sp}/C=0.0188$ $[1+A\zeta^2/\lambda_1$ where $A\zeta^2/\lambda_1=1.01$. It may be pointed out that equation (3) assumes the aforesaid form when $\lambda_s=\lambda_1$. It may, therefore, be concluded that at the isoionic point of β-lactoglobulin $\lambda_s=\lambda_1$ nearly when the NaCl content of the solution is 0.05 N.

The data recorded in Table 4 show that in the absence of NaCl and at *p*H 4.22 ± 0.05, η_{sp}/C of β-lactoglobulin decreases as C increases. This is just the opposite of what has been observed in the case of ESA and ribonuclease and is to be attributed to the absence of NaCl so that in equation (3) λ_1 is much less than λ_s and C in the numerator is negligible compared to K_0. Equation (3) then assumes the following approximate form which fits the data,

$$\eta_{sp}/C=0.0188\left[1+\frac{6.2}{C+3}\right].$$

It may be noticed that m, the electrophoretic mobility, recorded in Table 4 decreases markedly as C increases. This marked decrease in m cannot be accounted for by the increase in viscosity caused by the increase of C. The mobility data obviously require surface conductance or elaborate relaxation correction[14]. Therefore, based on such uncorrected data, Briggs remarks on the validity of the electroviscosity equation of Smoluchowski are not of much significance.

The data on isoionic solutions of BSA and ribonuclease recorded in the Tables 5 and 6 show that for different values of S, the observed values of R agree satisfactorily with those calculated by using equation (6).

The data recorded in the Tables 7 and 8 also show that the variation of R of β-lactoglobulin with S of NaCl can be accounted for quantitativity by

TABLE 7

VARIATION OF R OF β-LACTOGLOBULIN AT *p*H 4.22±0.05

Miscellaneous	S	η_{sp}	Values of R Observed	Values of R Calculated
C=0.5 per cent	0	0.0256	1.0	1.0
Equation used (6)	0.0005	0.0237	0.926	0.895
m=0.26	0.001	0.0217	0.848	0.851
m_0=00074	0.002	0.0206	0.805	0.810
	0.005	0.0196	0.766	0.774
	0.01	0.0193	0.754	0.758
C=1 per cent	0	0.0468	1.0	1.0
Equation used (6)	0.0005	0.0451	0.963	0.948
	0.001	0.0430	0.919	0.919
m=0.19	0.002	0.0417	0.891	0.886
	0.005	0.0396	0.846	0.850
m_0=0.00134	0.01	0.0390	0.838	0.832
C=2 per cent	0	0.0886	1.0	1.0
Equation used (6)	0.0005	0.0870	0.982	0.975
	0.001	0.0847	0.956	0.956
m=0.187	0.002	0.0828	0.929	0.928
m_0=0.00324	0.005	0.0789	0.891	0.887
	0.01	0.0761	0.859	0.859

† Varying values from 0.71 to 0.75 are reported in the literature.

TABLE 8

VARIATION OF R OF β-LACTOGLOBULIN AT pH 6.60 ± 0.05

Miscellaneous	S	η_{sp}	Values of R	
			Observed	Calculated
C = 0.57 per cent	0	0.0327	1.0	1.0
Equation used (6)	0.001	0.0262	0.801	0.802
	0.002	0.0237	0.725	0.740
m = 0.38	0.005	0.0224	0.685	0.679
m_o = 0.00092	0.01	0.0213	0.651	0.652
C = 1.15 per cent	0	0.0582	1.0	1.0
Equation used (6)	0.001	0.0513	0.881	0.881
m = 0.275	0.002	0.0486	0.835	0.834
m_o = 0.00131	0.005	0.0458	0.787	0.782
	0.01	0.0440	0.756	0.757

equation (6). It may be pointed out here that when S is very small, say 0.0005 *M*, any adsorption of it by the protein lowers its value still further. If this lower value of S were known and used in equation (6) the agreement in this region would have improved appreciably. At pH 4.22 ± 0.05 three concentrations of β-lactoglobulin have been used and it may be noticed that m_o in equation (6) increases as C increases. This is in agreement with the theory, since $m_o = (C\lambda_s + K_o\lambda_i)/K_o\lambda_i h$ and so it should increase as C increases. Similar remarks apply to the two solutions of β-lactoglobulin at pH 6.60 ± 0.05. It may be pointed out that only the first order (i.e., the primary) electroviscous effect is operative in the range of protein concentration discussed above.

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Prototype Computation of Minimum Energy Conformation (MEC) to Explore the Active Receptor Sites

A. U. DE,*, A. K. GHOSE and ANJALI HORE

Department of Pharmacy, Jadavpur University, Calcutta-700 032.

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A routine computational procedure for determining the preferred molecular conformation cum molecular geometry through the minimisation of energy has been described. The method, inspite of its various shortcomings, is operationally simpler than the advanced quantum mechanical approaches. The procedure, though illustrated with a simple molecule like *n*-butane, can be extended either to the whole or to some selected portions of complex drug molecules to elucidate their preferred geometry providing a greater insight into the drug-receptor interaction at the molecular level. When applied to the well known neurotransmitter, acetylcholine, its predicted minimum energy conformation based on torsional, Van der Waals nonbonded interaction, and electrostatic energies, is in perfect agreement with the reported X-ray and NMR results. Studies on the existence of some suitable receptor sites for the anticancer drugs are in progress and the observations thereto will constitute the subject matter of some future communications. Computational work has been performed in B6700 computer at the Regional computer center, Calcutta.

STRUCTURAL and distance dependencies in drug-receptor interaction phenomenon is well known. Preferred molecular conformation of a drug molecule is immensely significant for the understanding of drug-receptor interaction at the molecular level ultimately leading to a greater understanding of structure-activity relationship, drug action mechanism and new drug design. As the pattern of essential atoms and groups in a drug molecule must have some distinct relationship to complementary features on the receptor molecule, the spatial relationship of these essential moieties may be a help to map the complementary features of a receptor. Several quantum mechanical approaches[1-3] like EHT, CNDO, SCF are already available to determine the preferred geometry of a molecule. On the contrary, the problem of minimum energy conformation[4] has been approached by Hendrickson[5], Ramachandran[6], and Liquori[7] independently from a different angle where the Partition of Energy Method (PEM) has been applied. The term PEM has been first coined by Liquori and seems to be appropriate for the purpose. In later stages, Scheraga and his associates[8-11] have not only improved the PEM, but have also combined it with quantum mechanical approaches to obtain a better picture of molecular conformation.

The approach followed by Hendrickson had greater flexibility as it incorporated the bond angle deformations and the subsequent complications arising therefrom in computing the dihedral angles. This feature has been ignored by the others as it seemed unimportant for their specific problems. In contrast to the others, Hendrickson did not follow any fixed coordinate system for the computation of nonbonded distances which rendered the process operationally simpler, although it required more storage space in the computer memory than the fixed coordinate system adopted by the others. While Hendrickson concentrated on the problem of various acyclic and cyclic hydrocarbons, the other workers paid attention to the biopolymers like protein, nucleic acid, carbohydrates, and other synthetic polymers. According to the PEM the total energy of a molecule is viewed as the combined sum of bond angle deformation energy, torsional energy, van der Waals nonbonded interaction energy (i.e., the algebraic sum of attractive and repulsive energies), electrostatic energy, bond deformation energy, hydrogen bond energy, hydrophobic interaction energy, libration energy and looping energy[12]. Computation of all these energy contributions and its subsequent minimisation leads to the minimum energy conformation of a molecule. However, the preferred conformation of a biologically active molecule need not be in the stable state of minimum energy but rather in a metastable state of somewhat higher energy lying in the neighbourhood of the minimum energy conformation. Technological advances have not only made it possible to compute energies of various conformations of a molecule, but also to view its three dimensional picture on a computerised oscilloscope screen simultaneously[13]. As all these procedures need extensive computation, various approximations have been exercised by the workers to minimise it by the judicious choice of the main contributing factors to the total energy. For example, in some cases[5] a number of van der Waals interaction energy terms have been overlooked to incorporate various angle strain energies. Whereas in some cases van

der Waals interaction energy and torsional energy terms have been emphasized but the angle strain and electrostatic energies have been ignored. While considering a biologically active molecule *in vivo* both the hydrogen bond energy and hydrophobic interaction energy need be considered in addition to the usual angle strain, torsional, van der Waals interaction and electrostatic energies. In the present case, a general programme has been furnished enabling its broader application by an intending investigator.

The most significant feature of conformational energy computation by PEM is the determination of various nonbonded distances of a particular molecule. The different nonbonded distances are functions of (i) bonded distances, d, which are usually assumed to be constant, (ii) bond angles, θ, and (iii) dihedral angles, ω. It is evident that the geometry and energy of a particular conformation are mainly determined by θ's and ω's. Explicit expressions correlating these variables with energies based on parameterisation are already available[5,11,14]. As there are six θ's around each carbon atom, and nine ω's around each C – C bond, the conformation of a molecule is complicated by a large number of θ's and ω's. But, fortunately, all these θ's and ω's are not independent. Thus when the C – C – C bond angle is defined (either normal or distorted), the remaining five bond angles around the central carbon atom are automatically fixed up. For a 10° deviation from normal bond angle, the distorted θ's and their projections on the plane perpendicular to the C – C bond can be calculated by the formalism* of Hendrickson as reported earlier[5,14]. Some of these θ's, for reasons of symmetry or equivalent substitutions, may be identical which reduce the number of calculations. The projection angles are necessary for evaluating the dihedral angles between any two bonds.

In the present case, the practice of denoting the dihedral angle with a positive sign for anticlockwise rotation and negative sign for clockwise rotation has been discontinued. Here, the dihedral angle is determined always with an anticlockwise rotation, and hence with a positive sign. The Newman projection (Fig.1) will illustrate the point :

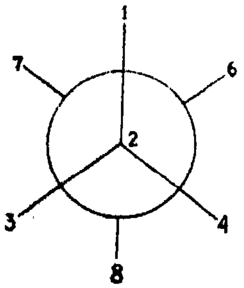


Fig 1.

$$\omega_{4,8} = P_{4,1} + P_{7,8} + \omega_{1,7} \quad \ldots \quad (1)$$

$$\omega_{3,6} = P_{3,4} + P_{4,1} + \omega_{1,7} + P_{7,8} + P_{8,6} \quad \ldots \quad (2)$$

where, $\omega_{4,8}$, $\omega_{1,7}$, $\omega_{3,6}$ are the dihedral angles corresponding to the atoms denoted by the subscripts ; $P_{4,1}$, $P_{7,8}$, $P_{3,4}$, $P_{8,6}$ are the projection angles corresponding to the atoms denoted by the subscripts ; $\omega_{1,7}$ has any arbitrarily assigned value. By this procedure any other dihedral angle can be evaluated. It is evident from the above discussion that the fixation of one θ around each carbon atom and one ω around each C – C bond completely defines each conformation. All these points will be further clarified with the example of *n*-butane in which case the Ficher's projection formula (Fig. 2) is written first and all the atoms are specified with a number in successive manner for computational advantage.

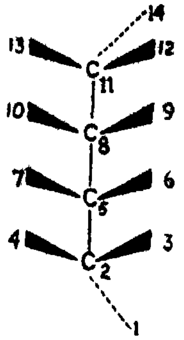


Fig 2.

As it is a four carbon system the complete geometrical picture of this molecule is defined by 4 × 6, i. e., 24 θ's, six around each carbon atom and (4 – 1) × 9, i. e. 27 ω's, nine around each C – C bond. Amongst this large number of θ's and ω's only four θ's, one around each carbon atom, and three ω's, one around each C – C bond, need be specified, i.e., they are assumed to behave independently when the other twenty θ's and twentyfour ω's are automatically specified. In the present cose say, $\theta_{1,5}$, $\theta_{2,8}$, $\theta_{5,11}$, $\theta_{8,14}$ and $\omega_{1,8}$, $\omega_{2,11}$, $\omega_{5,14}$ are assumed to be independent, and all other θ's and ω's are evaluated by the explicit expressions*.

The next step in getting the conformational picture is to calculate the energy of each conformation. The angle strain energy is the combined sum of the twentyfour strain energies due to these twentyfour θ's. The torsional strain energy is calculated either as the simple combined sum of three strain energies due to the three independent ω's or as the combined sum of three individual averages of nine strain energy terms around each C – C bond corresponding to the twenty-seven ω's. But the most difficult problem is to compute all the nonbonded interactions comprising of carbon-carbon, carbon-hydrogen, hydrogen-hydrogen interactions, since for such computations all the nonbonded distances need be calculated first. The total number of nonbonded distances in acyclic saturated hydrocarbons is given by $N/2 \times (N-1) - (3N_c + 1)$, where N is the total number of atoms and N_c is the number of carbon atoms only. The first term actually gives the total number of internuclear distances and the second term gives the number of

* Details may be obtained on request from the authors.

TABLE 1—REQUIRED SPECIFIC VARIABLES FOR COMPUTATION

n=2	n=3			n=4			n=5			n=6		
$r_{1,2}$ $d_{1,2}$	$r_{1,3}$ $d_{2,3}$; $\theta_{1,3}$	$r_{1,4}$ $d_{2,4}$; $\theta_{1,4}$	$r_{1,5}$ $d_{2,5}$; $\theta_{1,5}$	$r_{1,6}$ $d_{5,6}$; $\theta_{2,6}$ $\omega_{1,6}$	$r_{1,7}$ $d_{5,7}$; $\theta_{2,7}$ $\omega_{1,7}$	$r_{1,8}$ $d_{5,8}$; $\theta_{2,8}$ $\omega_{1,8}$	$r_{1,9}$ $d_{8,9}$; $\theta_{5,9}$ $\omega_{2,9}$	$r_{1,10}$ $d_{8,10}$; $\theta_{5,10}$ $\omega_{1,10}$	$r_{1,11}$ $d_{8,11}$; $\theta_{5,11}$ $\omega_{2,11}$	$r_{1,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{1,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{1,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{5,14}$
$r_{4,2}$ $d_{4,2}$			$r_{4,5}$ $d_{2,5}$; $\theta_{4,5}$	$r_{4,6}$ $d_{5,6}$; $\theta_{2,6}$ $\omega_{4,6}$	$r_{4,7}$ $d_{5,7}$; $\theta_{2,7}$ $\omega_{4,7}$	$r_{4,8}$ $d_{5,8}$; $\theta_{2,8}$ $\omega_{4,8}$	$r_{4,9}$ $d_{8,9}$; $\theta_{5,9}$ $\omega_{2,9}$	$r_{4,10}$ $d_{8,10}$; $\theta_{5,10}$ $\omega_{2,10}$	$r_{4,1}$ $d_{8,11}$; $\theta_{5,11}$ $\omega_{2,11}$	$r_{4,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{4,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{4,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{5,14}$
$r_{3,2}$ $d_{3,2}$		$r_{3,4}$ $d_{2,4}$; $\theta_{3,4}$	$r_{3,5}$ $d_{2,5}$; $\theta_{3,5}$	$r_{3,6}$ $d_{5,6}$; $\theta_{2,6}$ $\omega_{3,6}$	$r_{3,7}$ $d_{5,7}$; $\theta_{2,7}$ $\omega_{3,7}$	$r_{3,8}$ $d_{5,8}$; $\theta_{2,8}$ $\omega_{3,8}$	$r_{3,9}$ $d_{8,9}$; $\theta_{5,9}$ $\omega_{2,9}$	$r_{3,10}$ $d_{8,10}$; $\theta_{5,10}$ $\omega_{2,10}$	$r_{3,11}$ $d_{8,11}$; $\theta_{5,11}$ $\omega_{2,11}$	$r_{3,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{3,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{3,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{5,14}$
$r_{2,5}$ $d_{2,5}$	$r_{2,6}$ $d_{5,6}$; $\theta_{2,6}$	$r_{2,7}$ $d_{5,7}$; $\theta_{2,7}$	$r_{2,8}$ $d_{5,8}$; $\theta_{2,8}$	$r_{2,9}$ $d_{8,9}$; $\theta_{5,9}$ $\omega_{2,9}$	$r_{2,10}$ $d_{8,10}$; $\theta_{5,10}$ $\omega_{2,10}$	$r_{2,11}$ $d_{8,11}$; $\theta_{5,11}$ $\omega_{2,11}$	$r_{2,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{2,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{2,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{5,14}$			
$r_{7,5}$ $d_{7,5}$			$r_{7,8}$ $d_{5,8}$; $\theta_{7,8}$	$r_{7,9}$ $d_{8,9}$; $\theta_{5,9}$ $\omega_{7,9}$	$r_{7,10}$ $d_{8,10}$; $\theta_{5,10}$ $\omega_{7,10}$	$r_{7,11}$ $d_{8,11}$; $\omega_{7,11}$	$r_{7,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{7,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{7,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{5,14}$			
$r_{6,5}$ $d_{6,5}$		$r_{6,7}$ $d_{5,7}$; $\theta_{6,7}$	$r_{6,8}$ $d_{5,8}$; $\theta_{6,8}$	$r_{6,9}$ $d_{8,9}$; $\theta_{5,9}$ $\omega_{6,9}$	$r_{6,10}$ $d_{8,10}$; $\theta_{5,10}$ $\omega_{6,10}$	$r_{6,11}$ $d_{8,11}$; $\theta_{5,11}$ $\omega_{6,11}$	$r_{6,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{6,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{6,14}$ $d_{11,14}$, $\theta_{8,14}$ $\omega_{5,14}$			
$r_{5,8}$ $d_{5,8}$	$r_{5,9}$ $d_{8,9}$; $\theta_{5,9}$	$r_{5,10}$ $d_{8,10}$; $\theta_{5,10}$	$r_{5,11}$ $d_{8,11}$; $\theta_{5,11}$	$r_{5,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{5,12}$	$r_{5,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{5,13}$	$r_{5,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{5,14}$						
$r_{10,8}$ $d_{10,8}$			$r_{10,11}$ $d_{8,11}$; $\theta_{10,11}$	$r_{10,12}$ $d_{11,12}$, $\theta_{8,12}$ $\omega_{10,12}$	$r_{10,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{10,13}$	$r_{10,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{10,14}$						
$r_{9,8}$ $d_{9,8}$		$r_{9,10}$ $d_{8,10}$; $\theta_{9,10}$	$r_{9,11}$ $d_{8,11}$; $\theta_{9,11}$	$r_{9,12}$ $d_{11,12}$; $\theta_{8,12}$ $\omega_{9,12}$	$r_{9,13}$ $d_{11,13}$; $\theta_{8,13}$ $\omega_{9,13}$	$r_{9,14}$ $d_{11,14}$; $\theta_{8,14}$ $\omega_{9,14}$						
$r_{8,11}$ $d_{8,11}$	$r_{8,12}$ $d_{11,12}$; $\theta_{8,12}$	$r_{8,13}$ $d_{11,13}$; $\theta_{8,13}$	$r_{8,14}$ $d_{11,14}$; $\theta_{8,14}$									
$r_{12,11}$ $d_{12,11}$			$r_{12,14}$ $d_{11,14}$; $\theta_{12,14}$									
$r_{13,11}$ $d_{13,11}$		$r_{12,13}$ $d_{11,13}$; $\theta_{12,13}$	$r_{13,14}$ $d_{11,14}$; $\theta_{13,14}$									

bonded distances. In the case of a cyclic saturated system the number of bonded distances is 3 N_c and the expression is modified accordingly. Thus even in this simple case of *n*-butane, the total number of nonbonded distances is seventyeight. All these nonbonded distances along with the d's, θ's and ω's required for their calculations are given in Table 1.

This type of representation has many computational advantages. The various nonbonded distances such as between the first and third atoms, first and fourth atoms, first and fifth atoms, first and sixth atoms are expressed under the specific column heads like n = 3,4,5,6 respectively. These columns are so constructed as to accomodate more than one interaction term under a specific column head. Thus out of the seventyeight internuclear distance terms, $N_c \times 6$, i.e., 24 terms correspond to n = 3 interactions. $(N_c - 1) \times 9$, i.e., 27 terms correspond to n = 4 interactions; $(N_c - 2) \times 9$, i.e., 18 terms correspond to n = 5 interactions, and $(N_c - 3) \times 9$, i.e., 9 terms correspond to n = 6 interactions. Furthermore, in accordance with this scheme, the computation of coordinates cum distances of all the constituent members under a specific column head utilises the co-ordinate of the last member of the previous column head, e.g., computation of $r_{1,9}$, $r_{1,10}$, $r_{1,11}$ under the column head n = 5 will utilise the co-ordinates of $r_{1,8}$ only under the column head n = 4 which is simultaneously obvious from the Fischer's projection formula (Fig.2). The coordinates and the nonbonded distances are calculated by the simple recipes of eqns. 3-6 as follows:

$$x_{i,n,k} = d_{i,n-1,k} - x_{i,n-1,3} \cos \theta_{i,n-2,k} - y_{i,n-1,3} \sin \theta_{i,n-2,k} \cos \omega_{i,n-3,k} + z_{i,n-1,3} \sin \theta_{i,n-2,k} \sin \omega_{i,n-3,k} \quad \ldots (3)$$

$$y_{i,n,k} = x_{i,n-1,3} \sin \theta_{i,n-2,k} - y_{i,n-1,3} \cos \theta_{i,n-2,k} \cos \omega_{i,n-3,k} + z_{i,n-1,3} \cos \theta_{i,n-2,k} \sin \omega_{i,n-3,k} \quad \ldots (4)$$

$$z_{i,n,k} = y_{i,n-1,3} \sin \omega_{i,n-3,k} + z_{i,n-1,3} \cos \omega_{i,n-3,k} \quad \ldots (5)$$

$$r = \sqrt{(x_{i,n,k})^2 + (y_{i,n,k})^2 + (z_{i,n,k})^2} \quad \ldots (6)$$

where, i = row index, n = column index, k = constituent member index.

As per this scheme, $x_{i,1,3} = 0, y_{i,1,3} = 0, z_{i,1,3} = 0$, $x_{i,2,3}$ = bonded distance between the first and second atom recorded under the column head n = 2, $y_{i,2,3} = 0$, $z_{i,2,3} = 0$. The subsequent calculations for n = 3 and onwards utilising the required d's, θ's and ω's are straightforward (eqns. 3-6).

The above mentioned four θ's and three ω's constitute a single set of seven independent angles. To get the complete conformational picture, each of these angles need be changed arbitrarily with judicious choice and the corresponding angle strain energy, torsional energy and nonbonded interaction energies are computed. Thus for the k variations of m θ's and l variations of n ω's the total number of sets is $k^m \times l^n$. The enormity of this calculation as per this general scheme is self-evident which, however, can be simplified by some rational assumptions. For instance, to preserve the C_2 axis of symmetry bisecting the $C_8 - C_8$ bond and $\omega_{8,11}$ dihedral angle in *n*-butane, it may be assumed that $\theta_{1,8} = \theta_{8,14}$, $\theta_{2,8} = \theta_{8,11}$ and $\omega_{1,8} = \omega_{5,14}$. This reduces the number of variables and consequently simplifies the calculation. On the other hand, the choice of optimum number of k's and l's, i.e., choice of the values of θ's and ω's reduces the number of sets and their calculations. But a drastic simplification without introducing any appreciable error is possible in an open chain system by assuming all the θ's as normal bond angles (109.47°) which renders all the projection angles as 120°. This assumption is somewhat true in all cases excepting cyclic systems and yield more or less satisfactory results. Application of the last simplifying assumption to the case of *n*-butane leads to a simpler array in terms of only d's and ω's. Only two variations of three ω's, 0 and 180°, leading to 2^3 sets have been considered in the present calculations. Energies of some conformations are given in Table 2.

TABLE 2—ENERGIES OF VARIOUS CONFORMATIONS OF *n*-BUTANE

$\omega_{1,8}$	$\omega_{8,11}$	$\omega_{5,14}$	E K cal/mole
0	0	180	16.14
0	180	0	6.50
0	180	180	3.02
180	0	180	5.40
180	180	180	0

To test the usefulness of this procedure, it was applied to the well known neurotransmitter acetylcholine as some experimental[15,16] and theoretical[17-20] observations regarding its conformations were already available from the literature. The Fischer's projection of this molecule is given in Fig. 3. As the molecule contained a number of

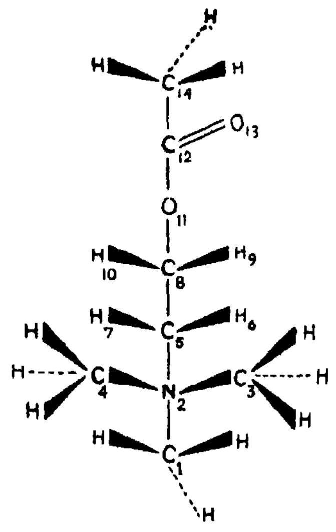


Fig. 3

‡ Details are available on request from the authors.

heteroatoms its electrostatic energy was also considered in addition to the usual torsional and van der Waals interaction energies.

All the number bearing atoms were taken into calculation and the others were ignored. The dihedral angles $\omega_{2,11}$ and $\omega_{5,12}$ were varied, but $\omega_{1,8}$ and $\omega_{8,14}$ were kept in a perfectly staggered form, since all the esters were known to have the rigid 'trans' form due to the delocalization of the electron pair on the ethereal oxygen. Furthermore, the electrostatic energy favours the 'trans' conformation over the 'cis' where also the delocalization has the same effect[21], Each of the two ω's were given twenty values (Table 3) leading to 20^2, i.e., 400 conformations. The values of $\omega_{2,11}$ were varied in between 0 and 180° in order to avoid calculation on some enantiomeric conformations. The dihedral angle $\omega_{5,12}$ was varied between 0 and 360°. When the electrostatic energy is considered in addition to the torsional and nonbonded van der Waals interaction energies, the minima around C_5-C_8 ($\omega_{2,11}$) was obtained at the gauche conformation (60-80°) in agreement with the X-ray and NMR results[15,16], but, not at 180° as earlier reported[17]. The minima around C_8-C_{11} ($\omega_{5,12}$) was found to be at 180° for the gauche conformation around C_5-C_8, although there were two more minima one at 70° having nearly 0.7 K cal/mole higher energy, and the other at 290° having nearly 1 K cal/mole higher energy over the minimum energy conformation. All these conformations have been observed crystallographically, although NMR suggested the value of 180° only. The energy of some important conformations are given in Table 4, while the entire conformational picture in illustrated in Figs. 4-6.

TABLE 3—DIHEDRAL ANGLES $\omega_{1,8}$ AND $\omega_{2,11}$ IN DEGREES

$\omega_{1,8}$	0	80	40	50	60	65	70	75	80	85
	90	100	110	120	130	140	150	160	170	180
$\omega_{2,11}$	0	30	40	50	60	70	80	90	120	170
	180	190	240	270	280	290	300	810	320	380

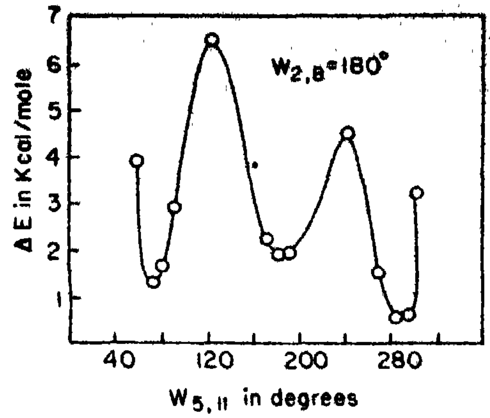


Fig. 5

TABLE 4—ENERGIES OF SOME CONFORMATIONS OF ACETYLCHOLINE

$\omega_{2,8}$	$\omega_{5,12}$	E K cal/mole
0	180	2.15
30	70	1.09
40	180	1.12
50	180	0.40
60	180	0
65	190	0.02
70	190	0.20
75	190	0.50
80	190	0.92
85	190	1.41
90	190	1.93
100	190	2.93
110	190	3.71
120	190	4.12
130	70	4.02
140	290	0.64
150	290	0.04
160	290	0.11
170	290	0.26
180	290	0.48

The nonbonded Van der Waals interaction energy was calculated with the help of equation (7), where a, μ and b

$$E = a\, e^{-\mu r} - b/r^6 \qquad (7)$$

are the van der Waals parameters (Table 5).

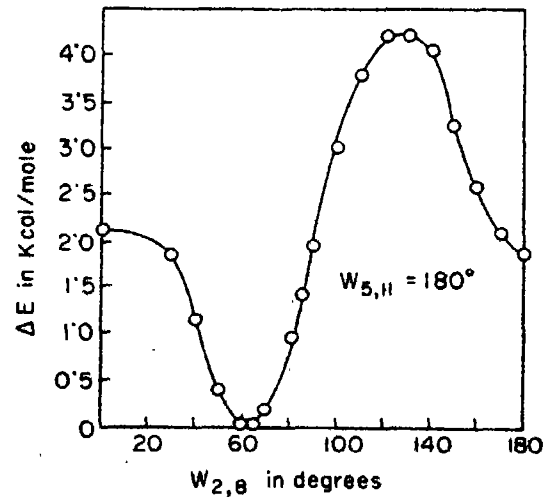


Fig. 4

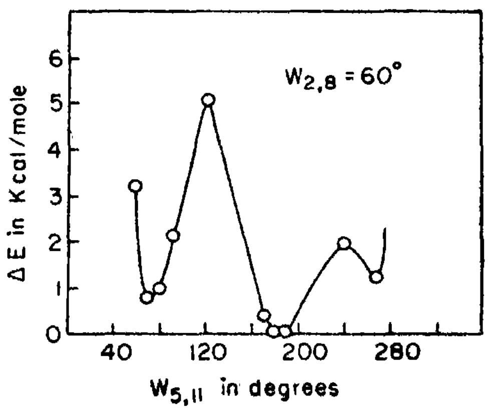


Fig. 6

TABLE 5—VALUES OF THE CONSTANTS USED IN CALCULATION OF VAN DER WAALS INTERACTION[14,26]

Atom pair	a	μ	b
HH	2800	3.6	49.2
HC	4012	3.4	125.0
HN	52160	5.0327	64.94
HO	57130	5.2247	47.97
CC	7000	3.2	325.00
CN	92800	4.2463	241.59
CO	91910	4.3821	221.70
NO	86940	4.686	140.56

The electrostatic energy was evaluated with the help of equation (8).

$$E_E = 331.9 \times e_1 \cdot e_2/D. \qquad \ldots \qquad (8)$$

where e_1 and e_2 are the point charges on the atoms expressed in the unit of electronic charge; D, the dielectric constant, was taken to be unity. The charges on the ester group were assigned from those of formic acid as obtained by the CNDO calculation by Pople[22] and the charges on the quaternary ammonium system were given from C–N dipole moment value which was taken as 1D[23] for the reasons that the MO calculations were somewhat controversial[20,21] and the hydrogens of the methyl groups were not included into calculations. The bond distances and charges of acetylcholine are given in Tables 6 and 7.

TABLE 6—BOND DISTANCES IN Å

$C_{sp^3}-H$	1.11	$C_{sp^3}-C_{sp^3}$	1.54	$C_{sp^2}-C_{sp^3}$	1.50
$C_{sp^3}-N$	1.47	$C_{sp^3}-O$	1.41	$C_{sp^2}-O$	1.34
$C_{sp^2}=O$	1.20				

TABLE 7—CHARGES ON THE VARIOUS ATOMS OF ACETYLCHOLINE

Atom	Charge	Atom	Charge
C_1, C_3, C_4, C_5	0.1414	N_2	0.4944
C_6	0.2	C_{12}	0.4
O_{11}	−0.265	O_{13}	−0.3

The torsional energy was evaluated with the help of equation (9):

$$E_T = 1.325 \quad (1+\cos \quad 3\omega_{2,11}) + 1.325/3 \quad (1+\cos \quad 3\omega_{6,12}).$$

The one-third value in the second term was due to the fact that only a single bond became eclipsed[24].

Computer Programming and Results :

A programme§ has been developed to calculate all the interactions taking into account the appropriate bond distances (d), bond angles (θ) and the dihedral angles (ω). Computation is repeated eight times for eight sets of ω's for *n*-butane, and four hundred times for four hundred sets of ω's for acetylcholine giving the internuclear distances, torsional strain energy, van der Waals interaction energy, electrostatic energy and total energy as printouts. The programme was written so as to compute the energies of only those conformations having all the nonbonded distances greater than 1.5Å. Some of the sets of *n*-butane happen to be identical which serve as a check for the reliability of computations. As θ's have been assumed to be nonvariant, the angle strain energy does not arise. Hence the total energy represents here the sum of torsional strain energy and van der Waals interaction energy for *n*-butane, and in addition electrostatic energy for acetylcholine.

Discussion :

The scheme represented above is a general one having the provisions for variations of all the independent θ's and ω's. But instead of varying all the θ's and thereby immensely complicating a calculation, it is more logical to vary only one or more θ's which correspond to the substituents other than hydrogen attached to the particular carbon atoms. In the case of acyclic molecules, the variation in θ's appear to be less relevant to the present authors. If this has been detrimental, here it has been amply compensated by the greater emphasis laid on all the nonbonded interactions and electrostatic energy which, however, have been overlooked by many earlier workers for simplifying the calculations. The general scheme represented above is applicable to the cyclic and branched systems of any size also. Furthermore, its versatility lies in the computer printout of all the internuclear distances which may be useful in locating any particular region of a drug molecule responsible for binding with the receptor site[11] as well as for some advanced theoretical calculations. It should be emphasized herewith that though the quantum mechanical procedure of CNDO offers a more refined approach for the computation of molecular geometry, it has also many inbuilt complications rendering it less adoptable for many purposes. Whereas the approach described here, inspite of its limitations, is simpler, straightforward and easily applicable. As the determination of biological activity itself has some margin of error, some loss of accuracy in the computation of preferred conformation due to certain simplifying rational assumptions may be overlooked. Once the minimum energy conformation of a molecule is determined, various quantum mechanical parameters like structural and energy indices can be computed with the help of Del Re's σ-electron[20], and Hoffmann's all valence electrons formalisms[1], the latter requiring the various internuclear distances to compute the Slater's overlap Matrix. All these are likely to throw a further insight into the problem of molecular geometry of a compound. Investigations on the preferred conformation of various anticancer drug molecules and that of the receptor are in progress and will be communicated from this laboratory in the future.

§ Details would be available on request from the authors.

Acknowledgements :

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Studies in the Stobbe Condensation : Migration of the Double Bond*

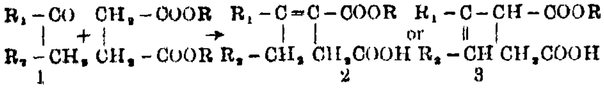
V. R. PASARKAR, B. H. PATWARDHAN and G. BAGAVANT*

Department of Chemistry, Nagpur University Campus, Nagpur-440 010.

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The Stobbe condensation of desoxybenzoin with dimethyl succinate, and of ∝-tetralone and cyclohexanone with diethyl homophthalate yield the corresponding alkylidene esteracids, 3-methoxycarbonyl-4,5-diphenylpent-3-enoic acid, ethyl 2-o-carboxyphenyl-2, 2-Δ'-tetralonylacetate and methyl 2-o-carboxyphenylcyclohexylidene acetate under mild reaction conditions. These ∝, β-unsaturated esters under more drastic experimental conditions lead to 3-methoxycarbonyl-4,5-diphenylpent-4-enoic acid, ethyl 2-o-carboxyphenyl-2-(3',4'-dihydro)-∝-naphthylacetate and methyl 2-o-carboxyphenyl-2-cyclohexenyl acetate by migration of the double bond forming the alkenyl systems.

THE Stobbe condensation[1] of ketones with succinic esters could yield alkylidene (2) or alkenyl products (3), if the ketone has a methylene group adjacent to it, and often a mixture is formed.



The condensation of desoxybenzoin ($1 : R_1 = R_2 = Ph$) with dimethyl succinate have been carried out by several workers[2,3,4] in presence of sodium ethoxide in ether, dry sodium ethoxide, and sodium hydride in benzene. They[2,3,4] reported the formation of a diacid ($3 : R_1 = R_2 = Ph$; $R = H$) m.p. 150-51°, the structure was based probably on the phenyl groups favouring a double bond in conjugation with them[5]. Effecting the Stobbe condensation in presence of butanolic potassium tert. butoxide under mild conditions of temperature (20 to 30°) and for a short period (30 to 50 min.) gave 3-methoxycarbonyl-4, 5-diphenylpent-3-enoic acid ($2 : R_1 = R_2 = Ph, R = Me$) m.p. 119°. When the condensation was conducted in refluxing tert. butoxide for 2.5 hr. it gave 3-methoxycarbonyl-4, 5-diphenylpent-4-enoic acid ($3 : R_1 = R_2 = Ph, R = Me$) m.p. 80°. Saponification of these acid esters yielded the corresponding diacids, m.p. 170° ($2 : R_1 = R_2 = Ph, R = H$) and m.p. 95° ($3 : R = R = Ph, R = H$) respectively. Structures could be definitely assigned to these compounds on the basis of their (i) equivalent weights and analytical data (ii) oxidation of ester-acid and diacid (3) with alkaline permanganate gave benzaldehyde facilely and instantaneously while the acid-ester and diacid (2) did not yield benzaldehyde on oxidation (iii) ir. spectrum of the carbonyl region of $2 : R = Me$ showed a single overlapped peak at 1710 cm^{-1} for an ∝,β-unsaturated ester and acid carboxyl (lit. 1730 – 1717 cm^{-1} and 1725 – 1700 cm^{-1})[1,6,7] whereas $3 : R = Me$ shows two peaks at 1710 cm^{-1} (saturated acid 1725 – 1700 cm^{-1}) and 1735 cm^{-1} (saturated ester 1750 – 1735 cm^{-1})[6,7].

Thus under mild conditions, the double bond is formed as would be expected from the condensation of the methylene of the succinic ester (viz.2) whereas under refluxing conditions, the double bond is in the migrated position as in (3). This migration of the double bond was further conclusively shown by refluxing the ester-acid ($2 : R = Me$) with butanolic potassium tert. butoxide when it was converted into ester-acid ($3 : R = Me$).

When the reaction was done under the reaction conditions of earlier workers[3] and the crude half-ester saponified *in situ*, it was observed that a diacid, m.p. 150-51° was obtained with the expected equivalent weight of 148, as reported. By crystallisation from benzene however, it could be easily separated into two different diacids ($2 : R = H$), m.p. 170° and ($3 : R = H$) m.p. 94°.

Lowenthal and Pappo[8] have reported the closely allied condensation of a Stobbe pattern in the reaction of diethyl homophthalate. For alternative double bond formation studies the tert. butoxide catalysed condensation of diethyl homophthalate and ∝-tetralone was investigated. In this reaction Chatterjea et al.[9] have found that the ethylenic double bond is situated in the alicyclic ring in conjugation with the aromatic ring (as in 7). When the reaction was conducted under the mild conditions as above ethyl-2-o-carboxyphenyl-2,-△'-tetralonylacetare (6 : R. Et) m.p. 163° was formed. Under the more drastic conditions of the reaction however, ethyl 2-o carboxyphenyl-2-(3',4'-dihydro)-∝-naphthyl acetate ($7 : R = Et$), m.p. 145° was formed. As in the earlier case the structural assignment could be made on the spectral and chemical data (see experimental). The migration was also effected by refluxion of the acid ($6 : R = Et$) with alkoxide when $7 : R = Et$ was obtained.

In the condensation of cyclohexanone and diethyl homophthalate, the viscous half-ester

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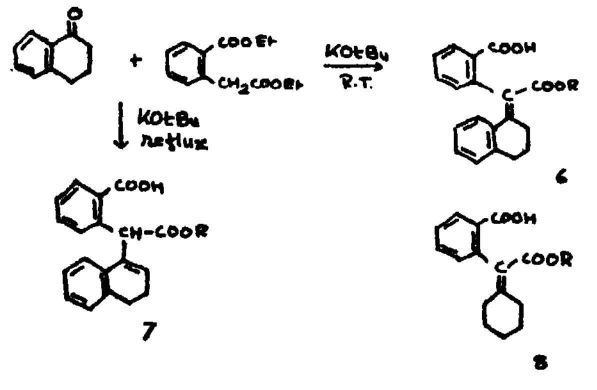
obtained under the milder conditions largely solidified to yield ethyl 2-*o*-carboxyphenylcyclohexylidene acetate (8 : R=Et), m.p. 111°. This on refluxing with potassium tert. butoxide gave an uncrystallisable oily mixture of half-esters[8] from which the diacids could be obtained as reported by Lowenthal and Pappo[8]. Thus, in this case, though the alkylidene system is the major product, the alkenyl system cannot be obtained easily for the initial system is also the thermodynamically stabler one.

The experiments indicate that the primary product in the Stobbe reaction is the alkylidene system, the alkenyl compound getting formed in a secondary double bond migration step which occurs only under more drastic conditions of refluxing alkoxide, Refluxing hydroxide does not result in migration but only in saponification.

Experimental

Stobbe Condensation with Desoxybenzoin :

A. Desoxybenzoin (19.6 g) and dimethyl succinate (16 g) were added to butanolic potassium tert. butoxide (from 4 g. potassium and 120 ml. butanol) and stirred magnetically under inert anhydrous conditions for 40 min. Then the reaction mixture was poured in ice-cold 3N-hydrochloric acid. The separated solid was filtered and taken up in benzene. The filtrate was extracted in benzene. The combined organic layers were repeatedly extracted with sodium carbonate solution. The alkaline solution on acidification gave *3-methoxycarbonyl-4, 5-diphenylpent-3-enoic acid*



(2 : $R_1 = R_2$ = Ph, R = Me) (5.7 g), crystallized from ether petroleum ether, m.p. 119° ; found : eq.wt. 309 ; C,73.2 ; H, 5.6. reqd. for $C_{19}H_{18}O_4$, eq.wt. 310 ; C,73.5 ; H,5.8%, uv : λ_{max}^{EtOH} 235 nm., log ϵ 4.11 ; ir : 1710 cm^{-1}(α,β-unsaturated ester and acid carboxyl). When treated with alkaline potassium permanganate, the permanganate got slowly decolourised but no benzaldehyde was formed.

Desoxybenzoin (9.8 g) and dimethyl succinate (7.3 g) were added to butanolic potassium tert. butoxide (from 2 g. potassium and 60 ml. butanol) and refluxed for 2.5 hr. The reaction mixture was cooled and poured in ice-cold 3N-hydrochloric acid, and the product worked up as before. The alkaline layer on acidification gave 3-methoxycarbonyl-4,5-diphenylpent-4-enoic acid (3 : $R_1 = R_2$ = Ph, R = Me) (7 g), crystallised from benzene-petroleum ether, m.p. 80° ; found : eq. wt. 309 ; C, 73.2 ; H, 5.9 ; reqd. for $C_{19}H_{18}O_4$, eq.wt. 310 ; C,73.5 ; H,5.87% ; uv : λ_{max}^{EtOH} 223, 253 nm, log 4.06 ; ir : 1710 and 1735 cm^{-1} (acid and ester). On treatment with alkaline potassium permanganate it gave a strong smell of benzaldehyde. After partial oxidation the material was extracted with ether and the solvent was removed, addition of alcoholic solution of 2,4-dinitrophenylhydrazine and sulphuric acid yielded the 2,4-dinitrophenylhydrazone, mixed m.p. 235°.

The acid-ester (1 g) was refluxed with 8% aq. sodium hydroxide (25 ml) for 6 hr. On acidification, it gave 3-carboxy-4, 5-diphenylpent-4-enoic acid (3 : $R_1 = R_2$ = Ph, R = H) (0.9 g), crystallized from rectified spirit, m.p. 94° ; found : eq.wt. 149 ; C, 72.6 ; H,5.6 ; reqd. for $C_{18}H_{16}O_4$, eq.wt. 148 ; C, 72.9 ; H,5.4% ; uv : λ_{max}^{EtOH} 226, 257 nm, log 4.13, 4.06. With alkaline potassium permanganate it gave a smell of benzaldehyde, which was identified through its 2,4-dinitrophenylhydrazone as above.

Isomerization of 3-methoxycarbonyl-4,5-diphenylpent-3-enoic acid with refluxing potassium tert, butoxide. 3-Methoxy carbonyl-4,5-diphenylpent–3 enoic acid (0.5 g) was mixed with butanolic potassium tert. butoxide (from 0.5 g potassium and 15 ml tert. butanol) and refluxed for 2.5 hr. The reaction mixture on working up as above gave 3-methoxycarbonyl-4,5-diphenylpent-4-enoic acid (0.4 g), crystallized from ether-petroleum ether, m.p. and m.m.p, 80°.

Stobbe Condensation of α-tetralone and diethyl homophthalate :

α-Tetralone (3.7 g) and diethyl homophthalate (5 g) were added to butanolic potassium tert. butoxide (from 1 g. potassium and 30 ml. butanol) and stirred magnetically under inert anhydrous conditions for 50 min. The reaction was worked up as usual when *ethyl 2-o-carboxyphenyl-2,2,-Δ^{1}-tetralonyl acetate* (6 : R=Et) (5.9 g) was obtained. It was crystallized from benzene-petroleum ether, m.p. 163°, found : eq. wt. 333 ; C,74.8 ; H, 6.1, reqd. for $C_{21}H_{20}O_4$. eq. wt. 336 ; C, 75 ; H, 5.95% uv : λ_{max}^{EtOH}. 244, 275 nm, log ϵ 3.89,4.03 g ; ir 1670 and 1715 cm^{-1} (aryl carboxyl and α,β-unsaturated ester).

Saponification gave the diacid (6 : R=H) m.p. 204° ; eq. wt. found : 151 ; reqd : 153 ; uv : λ_{max}^{EtOH} 252-256 nm, log ϵ 4.04 ; ir : 1670 cm^{-1} (aryl carboxyl and α,β-unsaturated acid).

Stobbe condensation with cyclohexanone : A mixture of cyclohexanone (2.5 g.), diethyl homophthalate

(5.9 g.) and potassium tert. butoxide (from 1 g. potassium and 30 ml. butanol) was stirred at 30° for 45 min. The reaction mixture was poured into ice-cold 3N-hydrochloric acid, extracted with ether, and the ethereal solution extracted with ice-cold sodium carbonate solution. The alkaline phase was acidified and the oily material got, on trituration with benzene-petroleum ether gave methyl *2-o-carboxyphenylcyclohexylidene acetate* (8 : R=Et) (7 g.), m.p. 109°, crystallized from ether-petroleum ether m.p. 112°; eq.wt. found : 286 ; reqd. for $C_{17}H_{20}O_4$, 288.

Saponification of the ester-acid (1 g) gave the cyclohexylidene diacid (8 : R=H), m.p. 188° (rectified spirit) lit[8] 183-4° eq.wt. found : 131 ; reqd. 130.

Isomerisation of the acid-ester (4 g.) with refluxing tert. butoxide (from 0.5 g potassium and 15 ml butanol), on working up in the usual way yielded an oil (3.8 g) which did not crystallise. This oil on saponification gave a diacid (3.0 g) which on crystallisation from acetic acid gave the diacid, m.p. and m.m.p. 188° (1.8 g) and the filtrate yielded the diacid, m.p, 140-2° (0.5 g) lit[9], 141-5°.

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Synthesis of Some Substituted Pyrazoles as Possible Antibacterial Agents

N. N. JOSHI and V. V. NADKARNY

Nadkarny-Sacasa Research Laboratory, St. Xavier's College, Bombay-400 001.

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Some pyrazole derivatives of the type II-VI were synthesised from 4-(3', 5'-Dimethyl-1'-pyrazolyl) benzhydrazide (I) and tested against *S. aureus* and *E. coli*. Only type III-compounds completely inhibited the growth of *S. aureus* at the concentrations employed.

THIOSEMICARBAZIDES have been reported to possess antitubercular[1] and antifungal[2] activity. Triazole nucleus itself has been associated with diverse biological activities[3], while some oxadiazoles show pesticidal properties[4]. Hence it was thought of interest to prepare some thiosemicarbazides, triazoles, oxadiazoles and thiadiazoles in order to study their antibacterial activities.

3,5-Dimethyl-1-(*p*-carboxyphenyl)-1(H) pyrazole[5] on esterification followed by treatment with hydrazine hydrate yielded the hydrazide (I) which on condensation with aromatic aldehydes, gave the corresponding N-benzylidene derivatives (II). Thiosemicarbazides (III) were obtained by condensing aryl isothiocyanates[6] with I. III on cyclization with aqueous alkali[7,8] gave the desired triazoles (IV) while with Iodine and alkali, the oxadiazoles (V) were obtained. Thiadiazoles (VI) were prepared by cyclizing III with concentrated sulphuric acid[9].

Compound V (Ar = phenyl) was also synthesised alternatively, by condensing I with Phenylisocyanate followed by cyclization with Phosphorus oxychloride. IR-spectra of the two products were superimposable and mixture—m.p. did not show any depression.

Experimental

All the mps. are recorded by open-capillary method and are uncorrected.

4-(3',5'-Dimethyl-1'-pyrazolyl) benzhydrazide (I) :

3,5-Dimethyl-1-(*p*-carboxyphenyl)-1(H) pyrazole (15 g) was dissolved in ethanol (60 ml), saturated with HCl gas and refluxed for 12 hr. The mixture was then cooled, poured into ice-cold water (400 ml) and basified with $NaHCO_3$. The product was filtered, washed with cold water and dried in vacuum. The crude ester (m.p. 60-62°) was used as such without purification.

The ethyl ester (0.05 mole) and hydrazine hydrate (95%, 0.1 mole) were refluxed in ethanol (20 ml) for 12 hr, concentrated under reduced pressure and the solid obtained on cooling was filtered. It was crystallized from aq. methanol (10%), m.p. 88°, yield (9.2 g, 80%), [Found : C 62.54, H 6.33, N 24.08 ; $C_{12}H_{14}N_4O$ requires C 62.61, H 6.09, N 24.35%]

4-(3', 5'-Dimethyl.1-pyrazolyl) phenyl-N-benzilidinohydrazides (II......Table 1) :

Equimolar quantities of hydrazide (I) and an appropriate aromatic aldehyde were refluxed in ethanol for 2 hr. Addition of a few drops of acetic acid improved the yields. Product separated on cooling were filtered, washed with ether and crystallized from ethanol (yields 65-80%).

1-[p-(3',5'-Dimethyl-1'-pyrazolyl) benzoyl]-4-aryl thiosemicarbazides (III......Table 2) :

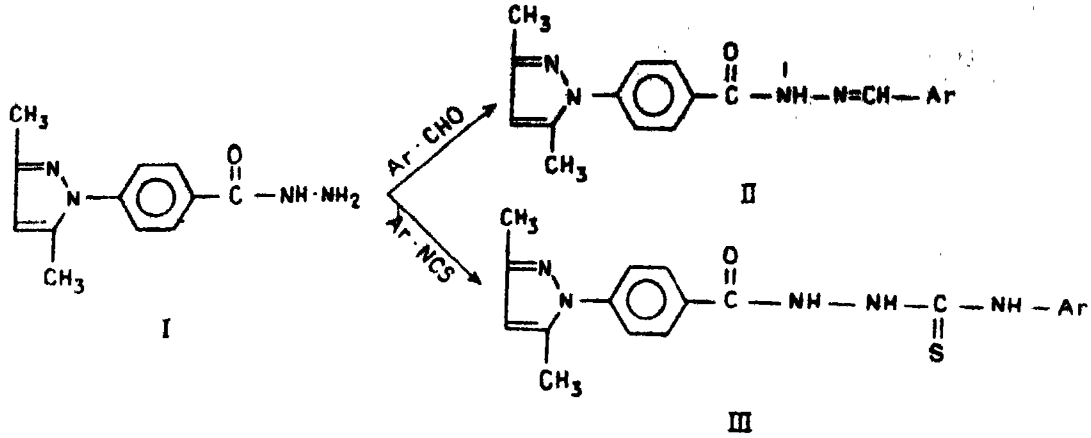
To a solution of I (0.01 mole) in ethanol (10 ml), was added with stirring an appropriate aromatic isothiocyanate (0.011 mole) in the same solvent (10 ml) and the mixture was refluxed for 3 hr. The solid product obtained on cooling was filtered, washed with ether and crystallized from ethanol (yields 75-85%).

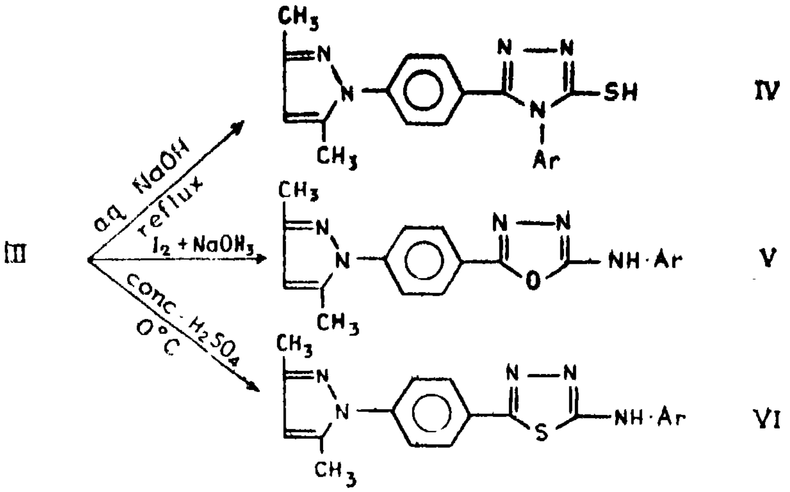
4-Aryl-3-mercapto-5-[p-(3',5'-dimethyl-1'-pyrazolyl) phenyl]-1,2,4-triazoles (IV......Table 3) :

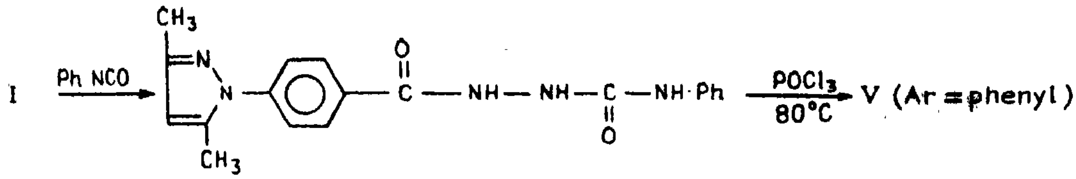
The thiosemicarbazide III (0.01 mole) and NaOH (2N, 40 ml) were refluxed for 2 hr. The solution was filtered, cooled and acidified with acetic acid. The solid product thus obtained was filtered, washed with water and crystallized aq. ethanol (yields 65-75%).

2-Arylamino-5-[p-(3',5'-dimethyl-1-1'-pyrazolyl) phenyl]-1,3,4-oxadiazoles (V......Table 4) :

Compound III (0.01 mole) was dissolved in a cold solution of NaOH (4 N, 5 ml). Iodine in KI (5%) was then added dropwise with stirring and cooling till the colour of Iodine persisted. The mixture was refluxed and more Iodine solution was added till a permanent tinge of Iodine remained. It was then cooled and poured in ice-cold water. The







precipitated solid was filtered, washed with a dil. $Na_2S_2O_3$ and then with water. The compound was crystallized from a 1 : 1 mixture of DMF-ethanol (yields 55-65%).

Alternatively, V (Ar = phenyl) was prepared by refluxing I (0.005 mole) and phenylisocyanate (0.006 mole) in alcohol (20 ml) for 6 hr. The product (VII) separated on cooling, was filtered, washed with cold methanol and crystallized from ethanol, m.p. 123°, yield (1.57 g, 90%).

The semicarbazide (VII) was heated with $POCl_3$ (10 ml) at 80 C for 4 hr. The liquid was cooled and poured over crushed ice. The solid obtained was filtered, washed with water and crystallized from a 1 : 1 mixture of DMF-ethanol, m.p. 240°, yield (1.02 g, 62%).

2-Arylamino,-5-[p-(3'.5'-dimethyl-1'-pyrazolyl) phenyl]-1,2,4-thiadiazole (VI......Table 5) :

The thiosemicarbazide II (0.01 mole) was added in small portions to conc. H_2SO_4 (100 ml) at 0°. The mixture was stirred at 0° for 3 hr. more. It was allowed to stand overnight at room-temperature and then poured over crushed ice. The precipitated solid was filtered, washed with oil. NH_4OH followed by water and crystallized from aq. methanol (yields 35-50%).

TABLE 1—4-(3′, 5′-DIMETHYL-1′-PYRAZOLYL) PHENYL-N-BENZYLIDINOHYDRAZIDE (II)

Sl. No.	Ar	M.P. °C	Mol. Formula	Analysis %N Calcd.	Analysis %N Found
1.	C_6H_5	233	$C_{19}H_{18}N_4O$	17.55	17.67
2.	2-OH.C_6H_4	197	$C_{19}H_{18}N_4O_2$	16.75	16.56
3.	4-OH.C_6H_4	159	$C_{19}H_{18}N_4O_2$	16.73	16.62
4.	4-OCH_3.C_6H_4	176	$C_{20}H_{20}N_4O_2$	16.05	15.93
5.	4-NO_2.C_6H_4	208	$C_{19}H_{17}N_5O_3$	19.12	18.97
6.	2-Furyl	118	$C_{17}H_{16}N_4O_2$	18.18	18.10

TABLE 2—1-[*p*-(3′,-5′-DIMETHYL-1′-PYRAZOLYL) BENZOYL]-4-ARYLTHIOSEMICARBAZIDES (III)

Sl. No.	Ar	M.P. °C	Mol. Formula	Analysis %S Calcd.	Analysis %S Found
7.	C_6H_5	118	$C_{19}H_{19}N_5OS$	8.77	8.98
8.	4-CH_3.C_6H_4	178	$C_{20}H_{21}N_5OS$	8.44	8.21
9.	4-Cl.C_6H_4	190	$C_{19}H_{18}N_5OSCl$	8.03	8.11

TABLE 3—4-ARYL-3-MERCAPTO-5-[*p*-(3′, 5′-DIMETHYL-1′-PYRAZOLYL) PHENYL]-1, 2, 4-TRIAZOLES (IV)

Sl. No.	Ar	M.P. °C	Mol. Formula	Analysis %S Calcd.	Analysis %S Found
10.	C_6H_5	271	$C_{19}H_{17}N_5S$	9.22	9.38
11.	4-CH_3.C_6H_4	245	$C_{20}H_{19}N_5S$	8.91	8.79
12.	4-Cl.C_6H_4	263	$C_{19}H_{16}N_5SCl$	8.39	8.61

TABLE 4—2-ARYLAMINO-5-[*p*-(3′, 5′-DIMETHYL-1′-PYRAZOLYL) PHENYL]-1, 3, 4-OXADIAZOLES (V)

Sl. No.	Ar	M.P. °C	Mol. Formula	Analysis %N Calcd.	Analysis %N Found
13.	C_6H_5	238	$C_{19}H_{17}N_5O$	21.18	21.03
14.	4-CH_3.C_6H_4	240	$C_{20}H_{19}N_5O$	20.41	20.11
15.	4-Cl.C_6H_4	260	$C_{19}H_{16}N_5OCl$	19.15	19.32

TABLE 5—2-ARYLAMINO-5-[*p*-(3′, 5′-DIMETHYL-1′-PYRAZOLYL) PHENYL]-1, 3, 4-THIADIAZOLES (VI)

Sl. No.	Ar	M.P. °C	Mol. Formula	Analysis %C Calcd.	Analysis %C Found
16.	C_6H_5	199	$C_{19}H_{17}N_5S$	9.22	9.31
17.	4-CH_3.C_6H_4	195	$C_{20}H_{19}N_5S$	8.91	9.03
18.	4-Cl.C_6H_4	225	$C_{19}H_{16}N_5SCl$	8.39	8.62

Screening for antibacterial activity

All the compounds from No. 1 to 18 were screened *in vitro* against *Staphyllococcus aureus* and *Escherichea coli* using concentration levels of 0.5, 1.0, 1.5 and 2.0 mg/ml. Compound nos. 7-9 completely inhibited the growth of *S. aureus* at all concentrations employed while compound nos. 1-6 were only effective at the level of 2 mg/ml. Except compound nos. 7-9 which slightly inhibited the growth at 2 mg/ml, none others were effective against *E. coli*.

Acknowledgement

The authors are grateful to UNICHEM Laboratories, Bombay, for microbiological testing of the compounds and also to Rev. Fr. L. Pereira, S.J., Principal, St. Xavier's College for providing the laboratory facilities.

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Possible Antiparkinsonian Compounds—Part XII Synthesis of Some Quinazolone Derivatives

V. K. PANDEY

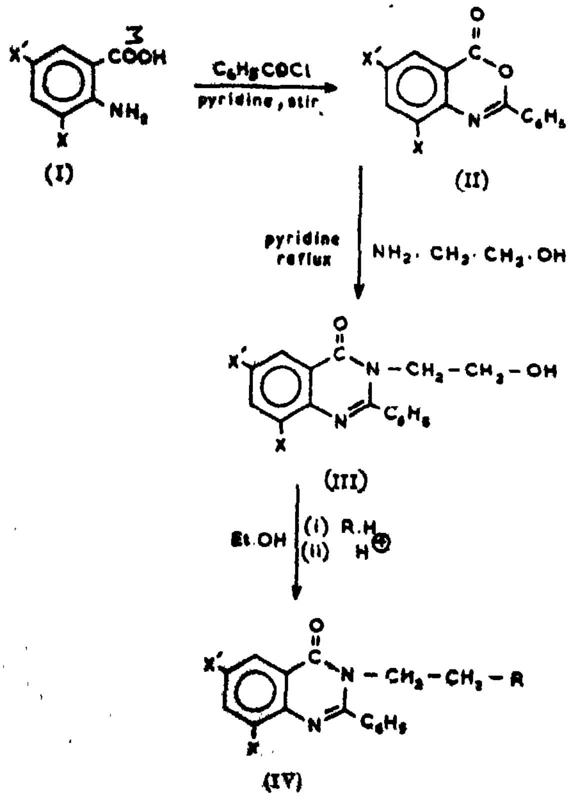
Department of Chemistry, Lucknow University, Lucknow.

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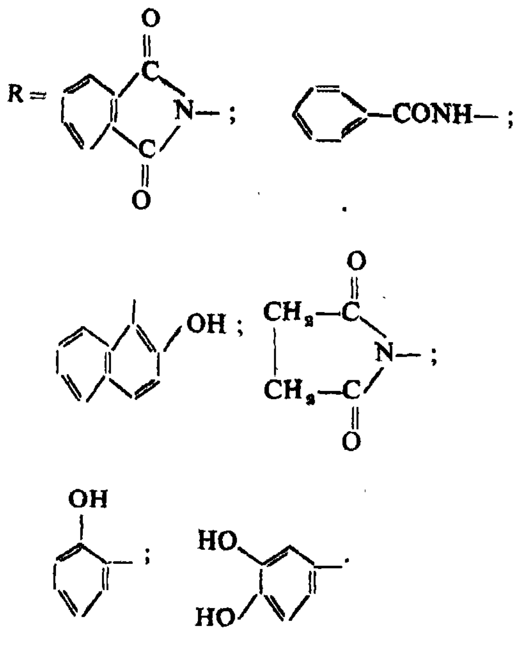
2-Aryl-3, 1(4H)-benzoxazin-(4)-one/2-aryl-6 : 8-dibromo-3, 1(4H)-benzoxazin(4H)-one/2-aryl-6-bromo-3, 1(4H)-benzoxazin(4)-one and monoethanolamine were condensed to yield 2-aryl-[3-(hydroxyethyl)]-3, 1(4H)-quinazolin-4-one/2-aryl-6 : 8-dibromo-[3-(hydroxyethyl)]-3, 1(4H), quinazolin-4-one/2-aryl-6-bromo-[3-(hydroxyethyl)]-3, 1(4H) quinazolin-4-one. These compounds were further condensed with the compounds containing active hydrogen atoms employing Mannich-reaction type method.

QUINAZOLONE derivatives show a wide variety of physiological and pharmacological properties such as central nervous system depressant[1-3], anticonvulsant[4,5], anticarcinogenic[6], musclerelaxant[6,7] and antiparkinsonian[8]. In view of these observations, it was thought worthwhile to synthesize some newer quinazolone derivatives with a view to testing their antiparkinsonian activity.

The synthesis was accomplished along the following route :



Where X = H ; Br



Experimental

All the melting points were taken in open capillaries in sulphuric acid melting point bath and are uncorrected.

5-bromo/3:5-dibromo-anthranilic acid (I) : This was obtained following the method of Rosanoff et al[9].

2-Phenyl-3,1-(4H)-benzoxazin-4-one/2-phenyl-6 : 8-dibromo-3,1-(4H)-benzoxazin-4-one/2-phenyl-6-bromo-3, 1-(4H) benzoxazin-4-one (III)

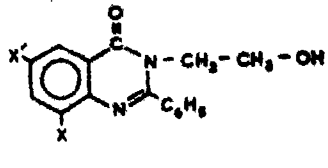
The procedure described by Sammour et al[11] was followed. Thus anthranilic acid/3 : 5-dibromo-anthranilic acid (0.01 mole) was dissolved in pyridine (30 ml). The solution was cooled and benzoyl-chloride (0.0 mole) was added dropwise with constant shaking. After the addition was complete, the mixture was further stirred for half an hour at room temperature. It was then treated with sodium bicarbonate solution (5%) to remove any unreacted acid. When the effervescence ceased, it was filtered and washed repeatedly with water in order to remove adhered pyridine. It was recrystallised from dilute ethanol.

2-Phenyl [-3-(hydroxyethyl)]-3,1 (4H)-quinazolin-4-one/2-phenyl-6 : 8-dibromo-[3-(hydroxyethyl)]-3.1 (4H)-quinazolin-4-one/2-phenyl-6-bromo-[3-(hydroxyethyl)]-3,1(4H)-quinazolin-4-one (III)

A mixture of 2-phenyl-3, 1 (4H)-benzoxazin-4-one/2-phenyl-6 : 8-dibromo-3, 1 (4H)-benzoxazin-4-one/2-phenyl-6-bromo-3, 1 (4H)-benzoxazin-4-one (0.01 mole) and monoethanol amine (0.01 mole) in 30 ml. of dry pyridine was refluxed for 6 hours and the reaction mixture was poured in ice cooled dil. HCl. The solid product that separated out, was repeatedly washed with water and recrystallized from dilute ethanol. Various compounds thus synthesized are recorded in Table 1.

2-Phenyl-3-(arylethyl) quinazolin-(3H)-4-one/2-phenyl-6 : 8-dibromo-3-(arylethyl)-quinazolin-(3H)-4-one/2-phenyl-6-bromo-3-(arylethyl)-quinazolin-(3H)-4-one (IV)

TABLE 1

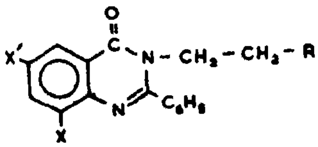


Sl. No.	X	X'	M. P.	Molecular formula	Analysis Calcd.	Analysis Found
1.	H	H	160	$C_{16}H_{14}N_2O_2$	10.50	10.23
2.	Br	Br	180	$C_{16}H_{12}N_2O_2Br_2$	6.01	6.21
3.	Br	H	194	$C_{16}H_{13}N_2O_2Br$	8.11	8.23

Note : The above compounds were recrystallised from ethanol. The yield ranged from 60-70%.

A mixture of the reactive hydrogen compound (0.005 mole), the above quinazolone (0.005 mole) (III) and a few drops of concentrated hydrochloric acid was dissolved in 30 ml. of ethanol and refluxed for 3 hours. After removing ethanol by distillation, a crude product was obtained, which was washed with water and then recrystallized from a polar solvent. The compounds thus synthesized are recorded in Table 2.

TABLE 2



Sl. No.	X	X'	R	M. P.°	Molecular formula	Analysis Nitrogen Calcd.	Analysis Nitrogen Found
1.	H	H	benzamido	174	$C_{23}H_{19}N_3O_2$	11.38	11.00
2.	H	H	phthalimido	170	$C_{24}H_{17}N_3O_3$	10.60	10.25
3.	H	H	succinimido	170	$C_{20}H_{17}N_3O_3$	12.10	11.85
4.	H	H	α-(β-naphthyl)	186	$C_{26}H_{20}N_2O_2$	7.10	7.66
5.	H	H	3 : 4-dihydroxyphenyl	180	$C_{22}H_{18}N_2O_3$	7.85	8.00
6.	H	H	α-(phenolyl)	178	$C_{21}H_{18}N_2O_2$		
7.	Br	Br	benzamido	195	$C_{23}H_{17}N_3O_2Br$	8.00	7.95
8.	Br	Br	(phenolyl)	192	$C_{22}H_{16}N_2O_2Br_2$	5.58	5.5
9.	Br	Br	α-(β-naphthyl)	189	$C_{26}H_{18}N_2O_2Br_2$	5.09	5.10
10.	Br	Br	succinimido	186	$C_{20}H_{15}N_3O_3Br_2$	7.98	7.51
11.	Br	Br	phthalimido	188	$C_{24}H_{15}N_3O_3Br_2$	7.76	7.22
12.	Br	H	succinimido	184	$C_{20}H_{17}N_3O_3Br$	9.83	9.52
13.	Br	H	phthalimido	175	$C_{24}H_{16}N_3O_3Br$	10.40	10.11

Note : The solvent used for the recrystallization was ethanol. The yield ranged from 50-60%.

Acknowledgement

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Synthesis of Substituted Arylhydrazones of 4-Aryl-4H-1,2, 4-Triazolyl-3-Thioacetic Acid Hydrazides

K. F. MODI, N. KRISHNAKUMAR, H. J. MEHTA, A. C. PADHYA and S. SOMASEKHARA

Sarabhai Research Centre, Wadi Wadi, Baroda-390 007

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Some 4-Aryl-4H-1, 2, 4-triazolyl-3-thioacetic acid hydrazides and their substituted arylhydrazones were prepared and screened for antibacterial, antituberculous and antifungal activities. These compounds showed weak antimicrobial activity.

ISONICOTINIC acid hydrazide (INH) and its derivatives are well known for their antituberculour activity[1]. Several 4H-1,2,4-triazole derivatives are also known to possess antimicrobial activity[2,3]. Accordingly, earlier we had prepared several 4-aryl-4H-triazolyl-3-thioacetic acids which had shown a weak antifungal activity[4]. It was also observed that some of the schiff bases prepared in this laboratory by condensing amines with halosalicylaldehydes had shown antimicrobial activity[5]. Hence as a part of our programme for finding potential antibacterial and antifungal agents, substituted arylhydrazones of 4-aryl-4H-1, 2, 4-triazolyl-3-thioacetic acid hydrazides were synthesised by the following sequence of reactions and they are reported here; but on screening none of them showed any significant expected activity at 50 mcg/ml level.

1. 4-Arylthiosemicarbazides were cyclised with ethylformate in presence of sodium methoxide to get 3-mercapto-4-aryl-4H-1,2,4-triazoles(I).

2. The mercapto triazoles(I) were reacted with ethylchloroacetate to give 3-thioacetic acid esters, which were further reacted with hydrazine hydrate to 4-aryl-4H, 1, 2, 4-triazolyl-3-thioacetic acid hydrazides(II).

3. The hydrazides(II) were reacted with substituted benzaldehydes to get the title compounds.

Experimental

Preparation of 4-Aryl-3-mercapto-4H-1, 2, 4-triazoles :

Prepared by the method as described in our communication reported earlier[4].

Preparation of 4-Aryl-4H-1,2,4-triazolyl-3-thioacetic acid hydrazides :

Prepared by the method described earlier[7]. 4-Aryl-3-mercapto-4H-1, 2, 4-triazoles (1 mol) in acetone were refluxed with ethylchloroacetate (2 mol) in presence of anhydrous sodium carbonate (4 mol) for 6 hours. The reaction mixture was cooled and filtered. The solvent and unreacted ethylchloroacetate were removed under reduced pressure to get crude 4-aryl-4H-1, 2, 4-triazolyl-3-thioacetic acid esters. These esters (1 mol) were further reacted with hydrazine hydrate (2 mol : 94-96%) in alcohol at room temperature to get clear solution. Within half an hour most of the hydrazides crystallised out. They were recrystallised from hot alcohol (50-55% yield).

Preparation of substituted Arylhydrazones of 4-aryl-4H-1,2,4-triazolyl-3-thioacetic acid hydrazides :

Prepared by the method described earlier[8]. 4-Aryl-4H-1,2,4-triazolyl-3-thioacetic acid hydrazides (1 mol) in alcohol were added to substituted benzaldehydes (1 mol) in alcohol in presence of acetic acid at 60-70°. On cooling the reaction mixture, the title compounds were obtained as crystalline solids. They were recrystallised from hot alcohol.

The compounds are listed in Tables 1-6.

TABLE 1

4-ARYL-4H-1, 2, 4-TRIAZOLYL-3-THIOACETIC ACID HYDRAZIDES

Sl. No.	R	M. P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	3-CH_3	159.61	$C_{11}H_{13}N_5OS$	26.5	26.6
2.	4-CH_3	144-46	$C_{11}H_{13}N_5OS$	27.0	26.6
3.	2-OCH_3	158-65	$C_{11}H_{13}N_5O_2S$	25.6	25.0
4.	3-OCH_3	170-72	$C_{11}H_{13}N_5O_2S$	24.9	25.0
5.	4-OCH_3	172-76	$C_{11}H_{13}N_5O_2S$	25.7	25.0
6.	2-Cl	168	$C_{10}H_{10}ClN_5OS$	24.9	24.6
7.	3-Cl	188-91	$C_{10}H_{10}ClN_5OS$	24.3	24.6
8.	4-Cl	164-67	$C_{10}H_{10}ClN_5OS$	24.0	24.6
9.	4-Br	170-72	$C_{10}H_{10}BrN_5OS$	21.4	21.3
10.	4-I	201-03	$C_{10}H_{10}IN_5OS$	18.9	18.3
11.	3-CF_3	157-59	$C_{11}H_{10}F_3N_5OS$	21.9	22.5
12.	2, 4-$(CH_3)_2$	167-70	$C_{12}H_{15}N_5OS$	26.5	25.2
13.	2-CH_3-4-Cl	144-47	$C_{11}H_{12}ClN_5OS$	24.0	23.5
14.	2-CH_3-5-Cl	185-37	$C_{11}H_{12}ClN_5OS$	22.9	23.5

* All the melting points are uncorrected.

TABLE 2

2-HYDROXYPHENYLHYDRAZONAS OF 4-ARYL-4H-1, 2, 4-TRIAZOLYL-3-THIOACETIC ACID HYDRAZIDES

Sl. No.	R	M. P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	3-CH_3	140-43	$C_{18}H_{17}N_5O_2S$	18.8	19.0
2.	4-CH_3	175-77	$C_{18}H_{17}N_5O_2S$	18.4	19.0
3.	2-OCH_3	236-40	$C_{18}H_{17}N_5O_3S$	18.4	18.2
4.	3-OCH_3	163-65	$C_{18}H_{17}N_5O_3S$	17.4	18.2
5.	4-OCH_3	207-12	$C_{18}H_{17}N_5O_3S$	17.7	18.2
6.	2-Cl	201-05	$C_{17}H_{14}ClN_5O_2S$	18.2	18.0
7.	3-Cl	161-63	$C_{17}H_{14}ClN_5O_2S$	18.8	18.0
8.	4-Cl	202-04	$C_{17}H_{14}ClN_5O_2S$	18.2	18.0
9.	4-Br	224-26	$C_{17}H_{14}BrN_5O_2S$	15.8	16.2
10.	4-I	247-49	$C_{17}H_{14}IN_5O_2S$	15.1	14.6
11.	3-CF_3	176-80	$C_{18}H_{14}F_3N_5O_2S$	16.8	16.8
12.	2, 4-$(CH_3)_2$	168-70	$C_{19}H_{19}N_5O_2S$	18.8	18.3
13.	2-CH_3-4-Cl	180-85	$C_{18}H_{16}ClN_5O_2S$	17.2	17.4
14.	2-CH_3-5-Cl	196-99	$C_{18}H_{16}ClN_5O_2S$	17.9	17.4

* All the melting points are uncorrected.

TABLE 3

3-HYDROXYPHENYLHYDRAZONES OF 4-ARYL-4H-1, 2, 4-TRIAZOLYL-3-THIOACETIC ACID HYDRAZIDES

Sl. No.	R	M. P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
**1.	H	243-45	$C_{17}H_{15}N_5O_2S$	19.4	19.8
**2.	2-CH_3	229-31	$C_{18}H_{17}N_5O_2S$	19.0	19.0
3.	3-CH_3	230-32	$C_{18}H_{17}N_5O_2S$	18.9	19.0
4.	4-CH_3	220-22	$C_{18}H_{17}N_5O_2S$	19.5	19.0
5.	2-OCH_3	229-32	$C_{18}H_{17}N_5O_3S$	18.6	18.2
6.	3-OCH_3	214-16	$C_{18}H_{17}N_5O_3S$	18.0	18.2
7.	4-OCH_3	204-07	$C_{18}H_{17}N_5O_3S$	18.6	18.2
8.	2-Cl	240-41	$C_{17}H_{14}ClN_5O_2S$	18.9	18.0
9.	3-Cl	230-32	$C_{17}H_{14}ClN_5O_2S$	17.9	18.0
10.	4-Cl	240-43	$C_{17}H_{14}ClN_5O_2S$	18.2	18.0
11.	4-Br	249-51	$C_{17}H_{14}BrN_5O_2S$	15.8	16.2
12.	4-I	242-44	$C_{17}H_{14}IN_5O_2S$	15.0	14.6
13.	3-CF_3	197-99	$C_{18}H_{14}F_3N_5O_2S$	16.5	16.8
14.	2, 4-$(CH_3)_2$	210-13	$C_{19}H_{19}N_5O_2S$	19.0	18.8
15.	2-CH_3-4-Cl	220-23	$C_{18}H_{16}ClN_5O_2S$	17.0	17.4
16.	2-CH_3-5-Cl	239-41	$C_{18}H_{16}ClN_5O_2S$	17.2	17.4

* All the melting points are uncorrected.
** V. Zotta, Ana Tataru, *Farmacia*, 1975, **23**(4), 193-6.

TABLE 4

4-HYDROXYPHENYLHYDRAZONES OF 4-ARYL-4H-1, 2, 4-TRIAZOLYL-3-THIOACETIC ACID HYDRAZIDES

Sl. No.	R	M. P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
**1.	H	252-54	$C_{17}H_{15}N_5O_2S$	19.4	19.8
**2.	2-CH_3	168-70	$C_{18}H_{17}N_5O_2S$	18.7	19.0
3.	3-CH_3	190-92	$C_{18}H_{17}N_5O_2S$	18.8	19.0
4.	4-CH_3	256-59	$C_{18}H_{17}N_5O_2S$	19.1	19.0
5.	2-OCH_3	248-50	$C_{18}H_{17}N_5O_3S$	17.7	18.2
6.	3-OCH_3	185-87	$C_{18}H_{17}N_5O_3S$	17.8	18.2
7.	4-OCH_3	212-14	$C_{18}H_{17}N_5O_3S$	17.8	18.2
8.	2-Cl	160	$C_{17}H_{14}ClN_5O_2S$	17.2	18.0
9.	3-Cl	208-11	$C_{17}H_{14}ClN_5O_2S$	18.5	18.0
10.	4-Cl	251-61	$C_{17}H_{14}ClN_5O_2S$	18.7	18.0
11.	4-Br	265-66	$C_{17}H_{14}BrN_5O_2S$	15.7	16.2
12.	4-I	265-67	$C_{17}H_{14}IN_5O_2S$	14.7	14.6
13.	3-CF_3	173-75	$C_{18}H_{14}F_3N_5O_2S$	16.5	16.8
14.	2, 4-$(CH_3)_2$	236-38	$C_{19}H_{19}N_5O_2S$	18.1	18.3
15.	2-CH_3-4-Cl	201-05	$C_{18}H_{16}ClN_5O_2S$	17.1	17.4
16.	2-CH_3-5-Cl	215-18	$C_{18}H_{16}ClN_5O_2S$	17.9	17.4

* All the melting points are uncorrected.
** V. Zotta, Ana Tataru, *Farmacia*, 1975, **23**(4), 193-6.

TABLE 5

2-HYDROXY-5-CHLOROPHENYLHYDRAZONES OF 4-ARYL-4H-1, 2, 4-TRIAZOLYL-3-THIOACETIC ACID HYDRAZIDES

Sl. No.	R	M. P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	H	218-20	$C_{17}H_{14}ClN_5O_2S$	18.5	18.0
2.	2-CH_3	194-96	$C_{18}H_{16}ClN_5O_2S$	17.6	17.4
3.	3-CH_3	183-85	$C_{18}H_{16}ClN_5O_2S$	17.5	17.4
4.	4-CH_3	220-22	$C_{18}H_{16}ClN_5O_2S$	18.1	17.4
5.	2-OCH_3	285-87	$C_{18}H_{16}ClN_5O_3S$	17.0	16.7
6.	3-OCH_3	248-49	$C_{18}H_{16}ClN_5O_3S$	17.1	16.7
7.	4-OCH_3	150-54	$C_{18}H_{16}ClN_5O_3S$	17.4	16.7
8.	2-Cl	248-50	$C_{17}H_{13}Cl_2N_5O_2S$	17.2	16.5
9.	3-Cl	193-95	$C_{17}H_{13}Cl_2N_5O_2S$	17.1	16.5
10.	4-Cl	219-22	$C_{17}H_{13}Cl_2N_5O_2S$	17.1	16.5
11.	4-Br	235-20	$C_{17}H_{13}BrClN_5O_2S$	15.1	15.0
12.	4-I	240	$C_{17}H_{13}ClIN_5O_2S$	15.8	13.6
13.	3-CF_3	196-98	$C_{18}H_{13}ClF_3N_5O_2S$	15.8	15.5
14.	2, 4-$(CH_3)_2$	200-01	$C_{19}H_{18}ClN_5O_2S$	17.1	16.8
15.	2-CH_3-4-Cl	215-17	$C_{18}H_{15}Cl_2N_5O_2S$	16.5	16.0
16.	2-CH_3-5-Cl	200-02	$C_{18}H_{15}Cl_2N_5O_2S$	16.4	16.0

* All the melting points are uncorrected.

TABLE 6

2-HYDROXY-5-BROMOPHENYLHYDRAZONES OF 4-ARYL-4H-1, 2, 4-TRIAZOLYL-3-THIOACETIC ACID HYDRAZIDES

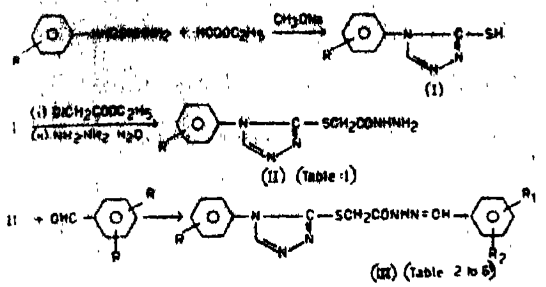
Sl. No.	R	M. P. °C*	Molecular Formula	Nitrogen % Found	Nitrogen % Calc.
1.	H	198-99	$C_{17}H_{14}BrN_5O_2S$	16.4	16.0
2.	2-CH_3	200-02	$C_{18}H_{16}BrN_5O_2S$	15.6	15.7
3.	3-CH_3	193-95	$C_{18}H_{16}BrN_5O_2S$	16.2	15.7
4.	4-CH_3	209-11	$C_{18}H_{16}BrN_5O_2S$	15.9	15.7
5.	2-OCH_3	225-27	$C_{18}H_{16}BrN_5O_3S$	15.0	15.1
6.	3-OCH_3	240-45	$C_{18}H_{16}BrN_5O_3S$	15.2	15.1
7.	4-OCH_3	165-66	$C_{18}H_{16}BrN_5O_3S$	15.4	15.1
8.	2-Cl	245	$C_{17}H_{13}BrClN_5O_2S$	15.2	15.0
9.	3-Cl	195-98	$C_{17}H_{13}BrClN_5O_2S$	15.0	15.0
10.	4-Cl	226-29	$C_{17}H_{13}BrClN_5O_2S$	15.6	15.0
11.	4-Br	240-44	$C_{17}H_{13}Br_2N_5O_2S$	14.2	13.5
12.	4-I	252-54	$C_{17}H_{13}BrIN_5O_2S$	13.0	12.5
13.	3-CF_3	208-10	$C_{18}H_{13}BrF_3N_5O_2S$	13.6	14.1
14.	2, 4-$(CH_3)_2$	202-05	$C_{19}H_{18}BrN_5O_2S$	15.8	15.2
15.	2-CH_3-4-Cl	212-15	$C_{18}H_{15}BrClN_5O_2S$	14.1	14.5
16.	2-CH_3-5-Cl	222-24	$C_{18}H_{15}BrClN_5O_2S$	14.6	14.5

* All the melting points are uncorrected.

Biological data

The *in vitro* antibacterial, antituberculous and antifungal activities were studied by the serial dilution method[6]. As the solutions of the compounds in dimethylformamide (DMF) and dilutions were made such that in no instance there was more than 1% DMF in the medium under study. It was confirmed that DMF at such concentrations had no inhibitory effect on the organisms under test. For antibacterial screening, the inoculated broth tubes were incubated at 37° for 24 hours and the dilution inhibiting the growth was noted. For antifungal screening, the inoculated broth tubes were inoculated at 27° and the state of growth was observed for 96 hours and the dilution showing no visible growth was noted. Antituberculous tests were carried out in Lownstien-

Jenson media. Results were recorded after three weeks incubation at 37° when tested at 50 mcg/ml concentration. These derivatives showed no inhibitory properties against the organisms.



(I) R=H ; 2-, 3-, 4-CH_3 ; OCH_3 and Cl ; 4-Br and I ; 3-CF_3 ; 2, 4-$(CH_3)_2$; 2-CH_3-4-Cl ; 2-CH_3-5-Cl

(II) R_1 = 2-, 3-, 4-OH ; R_2 = H

(III) R_1 = 2-OH ; R_2 = 5-Cl ; 5-Br.

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Studies in the Cyclohexane Series. Part XVIII. Ring Opening of the Anhydride of 1-Carboxy 3, 4-dimethyl-cyclohexane-1-acetic acid during Friedel-Crafts reaction and Synthesis of 2, 3-dimethyl-8, 9-benzo and Substituted 8, 9-benzospiro (5, 5) undecanes

R. K. GAUTAM and G. S. SAHARIA

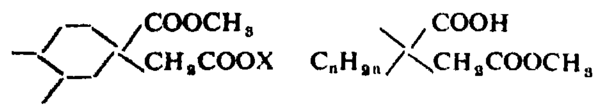
Department of Chemistry, University of Delhi, Delhi-110 007.

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The ring opening of the anhydride of 1-carboxy 3, 4 dimethyl-cyclohexane-1-acetic acid, m.p. 160° has been studied by converting the anhydride into the half-ester, its acid chloride and finally condensing it with benzene. The keto-ester so obtained on hydrolysis gave the keto-acid which was identical with the one obtained by the condensation of the anhydride with benzene under Friedel-Crafts reaction conditions.

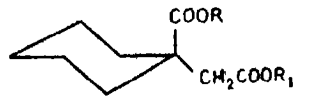
This anhydride was later condensed with toluene and isomeric xylenes to give the corresponding αα-(3′, 4′-dimethylcyclohexane)-β-aroylpropionic acids. All the keto-acids on catalytic reduction furnished αα-(3′, 4′-dimethylcyclohexane)-γ-aryl-n-butyric acids which on cyclisation with PPA followed by Clemmensen reduction yielded 2, 3-dimethyl-8, 9-benzo and substituted 8, 9-benzospiro (5, 5) undecanes.

IN order to determine the mode of opening of the anhydride ring during Friedel-Crafts reaction and confirm the earlier findings[1], the anhydride of 1-carboxy 3, 4-dimethylcyclohexane-1-acetic acid[2], m.p. 160° was converted into its half ester. This half ester was later converted into its acid chloride and subsequently subjected to Friedel-Crafts reaction with benzene. The keto-ester so obtained on hydrolysis furnished the keto-acid of the type IV (X=O) having m. p. identical with the one obtained by the Friedel-Crafts reaction of the anhydride with benzene and the mixed m.ps. of the two remained undepressed. Based on these reactions, the half ester has been assigned the structure I (X=H) and not of the type II as contended by some workers.[3]



I II

Further theoretical reasoning also renders support to the structure assigned ; of the two groups —COOH and —CH_2COOH present at C-1 in the molecules of the parent acid, the group —CH_2COOH being bulkier would occupy the equatorial position. The difference of free energy between the equatorial and axial —COOH and —$COOCH_3$ groups has been estimated to be 1.7 and 1.0 K cal/mole[4] respectively. On the basis of this free energy data IIIa would be stabler as compared to IIIb by 0.7 K cal/mole and therefore, the anhydride ring on opening would give the former.



III

a – $R=CH_3$; $R_1=H$

b – $R=H$; $R_1=CH_3$

Friedel-Crafts condensation of the anhydrides of 1-carboxy 4-, 3- and 2-methylcyclohexane-1-acetic acids with aromatic hydrocarbons has been reported[5]. With a view to study the bearing of disubstitution in the cyclohexane moiety on the analogous reaction and to compare this with unsubstituted and monosubstituted cyclohexane analogues, the condensation of the anhydride of 1-carboxy 3, 4-dimethylcyclohexane-1-acetic acid, m.p. 160° with benzene, toluene and isomeric xylenes has been carried out. In all these cases only one keto-acid, αα-(3′, 4′-dimethylcyclohexane)-β- aroylpropionic acid[5,6,7] of the type IV (X=O) was obtained ; the structures of these were confirmed by the formation of pyrylium salts and oxidation with sodium hypobromite to the known aromatic acids. These keto-acids were characterised by the formation of their 2, 4-DNPs, equivalent weight and I. R. spectral data (1690 cm^{-1} (ketone) and 1710 cm^{-1} carboxylic group).

During this condensation a small amount of a neutral product was always encountered which added up bromine and on the basis of elemental analysis and IR spectral data (1875 cm^{-1} correspon-

ding to βγ-unsaturated-γ-lactone) it has been assigned the lactonic structure[5,6,8]. The yield of the neutral product was greater in the case of isomeric xylenes than with benzene and toluene[5] and these were found to be dependent on temperature being minimum at 0-5°.

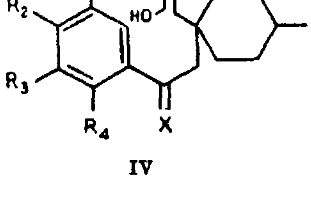
αα-(3′, 4′-Dimethylcyclohexane)-β-benzoylpropionic acid on Clemmensen reduction gave αα-(3′, 4′-dimethylcyclohexane)-γ-phenyl-n-butyric acid along with a small quantity of a neutral product. When this method of reduction was applied to the other keto-acids, the yields of the reduced acids diminished considerably and those of the neutral product increased to ~85%.

This difference in the reactivity of keto-acids towards Clemmensen reduction could be attributed to the presence of an additional methyl group in the cyclohexane moiety which may partly be responsible for the formation of the neutral product in larger amounts. This neutral product on the basis of analytical and I. R. spectral data (1775 cm^{-1} ; lactonic group) has been assigned a lactonic structure[5,6,8].

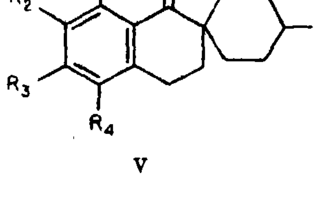
These keto-acids, however, could be reduced with palladium-charcoal (10%) under pressure to the corresponding butyric acids (IV ; $X=H_2$) in high yields (60-70%) and were characterised by elemental analysis, equivalent weight and I. R. spectral data (1710 cm^{-1}).

Our attempts to reduce the above keto-acids by modified Wolf-Kishner method[9] also did not meet with success as here again neutral products were obtaind (~90%) ; on the basis of elemental analysis and I.R. spectral data (1670 : ν C=O ; 3175 : ν N–H and 1610 cm^{-1} : ν C=N) these neutral products have been found to be present in the dimeric form of the monomer, a δ-lactam[5].

Cyclisation of the reduced acids with freshly prepared PPA[8] furnished the spiro-ketones of the type V(Y=O) characterised through their 2, 4 DNPs and I.R. peaks (1685 cm^{-1} : ν C=O). Their subsequent reduction by modified Clemmensen method furnished the corresponding spiro-hydrocarbons of the type V ($Y=H_2$).



IV



V

Experimental

1-Carbomethoxy 3, 4-dimethylcyclohexane-1-acetic acid

A solution of the anhydride of 1-carboxy 3, 4-dimethylcyclohexane-1-acetic acid, m.p. 160° (2 g) in absolute methanol (25 ml) was heated under reflux on a water bath (12 hrs). Excess of methanol was removed under vacuum, the residue taken up in ether, the ethereal solution washed with aqueous sodium carbonate (5% ; 4 × 30 ml) and the alkaline solution on acidification with dil. hydrochloric acid deposited an oil. This on distillation instead of the half ester gave the anhydride b.p. 164°/5 mm and, therefore, for subsequent work the undistilled product was employed. (Found : equiv., 227.2. $C_{12}H_{20}O_4$ requires 228.0 – monobasic). I.R. ν^{film}_{max} 1735 cm^{-1} (ester) and 1710 cm^{-1} (carboxylic group).

Acid chloride of 1-carbomethoxy 3, 4-dimethylcyclohexane-1-acetic acid

1-Carbomethoxy 3,4-dimethylcyclohexane-1-acetic acid (1.8 g ; 0.005 mole) and thionyl chloride (5 ml) were refluxed on a water bath (4 hrs). Excess of thionyl chloride was removed at water pump and the residue on distillation gave the *acid chloride of 1-carbomethoxy 3,4-dimethylcyclohexane-1-acetic acid*, b.p. 142°/11 mm, n_D^{36} 1.5216. (Yield : 81.5%). (Found : C, 56.6 ; H, 7.4 ; Cl, 14.1. $C_{12}H_{19}O_3Cl$ requires C, 56.8 ; H, 7.7 ; Cl, 14.3%). IR ν^{film}_{max} 1735 cm^{-1} (ester) and 1795 cm^{-1} (acid chloride).

Methyl αα-(3′,4′-dimethylcyclohexane)-β-benzoylpropionate

A solution of the above acid chloride (1.25 g ; 0.005 mole) in dry benzene was cooled in an ice-salt bath (0-5°) and anhydrous aluminium chloride (0.7 g ; 0.005 mole) added in small lots with shaking and cooling. The contents were kept in an ice-salt bath for 2 hours and left overnight at room temperature. The reaction mixture was heated in an oil bath at 60-70° (2 hours), and the complex decomposed with dilute hydrochloric acid ; on working up in the usual manner, *methyl αα-(3′,4′-dimethylcyclohexane)-β-benzoylpropionate* distilled at 156°/8 mm. n_D^{31} 1.5137. (Yield : 85.4%). (Found : C, 74.8 ; H, 8.2. $C_{18}H_{24}O_3$ requires C, 75.0 ; H, 8.3% I.R. ν^{film}_{max} : 1735 cm^{-1} (ester) and 1690 cm^{-1} (ketone).

αα-(3′,4′-Dimethylcyclohexane)-β-benzoylpropionic acid

The above ester (1.0 g) was refluxed with aqueous sodium hydroxide (10% ; 20 ml) (2 hours), the alkaline solution cooled, and acidified with concentrated hydrochloric acid. The deposited solid on crystallisation from benzene-petrol (60-80°) gave *αα-(3′,4′-dimethylcyclohexane)-β-benzoylpropionic acid*, m.p. 114°. (Yield : 71.3%).

(Found : C, 74.4 ; H, 7.8. equiv., 273.5. $C_{17}H_{22}O_3$ requires C, 74.5 ; H, 8.0% ; equiv., 274.0 monobasic).

Mixed m.p. of the above with the keto-acid obtained by the condensation of the anhydride of 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid,

m.p. 160° with benzene in the ratio (1 : 1) showed no depression.

The anhydride of 1-carboxy 3,4-dimethylcyclohexane-1-acetic acid m.p. 160°, obtained by refluxing it with acetic anhydride had b.p. 155°/4 mm. n_D^{27} 1.5314. (Yield : 90.0%).

(Found : C, 67.3 ; H, 8.0. $C_{11}H_{16}O_3$ requires C, 67.6 ; H, 8.2%).

Synthesis of 2,3-dimethyl-8,9-benzo and substituted 8,9-benzospiro (5,5) undecanes

αα-(3',4'-Dimethylcyclohexane)-β-aroylpropionic acids

To the cooled solution (0-5°) of the anhydride (3.92 g ; 0.02 mole) in dry hydrocarbon (25 ml) was added powdered anhydrous aluminium chloride (5.34 g ; 0.04 mole) in small lots during shaking. The reaction mixture was kept in an ice-salt bath for 2-3 hours, shaken vigorously at intervals, left at room temperature for 24 hours and then heated in an oil bath (60-70) for 2 hours. The complex was decomposed with ice-cold dilute hydrochloric acid, and on working up in the normal manner the above titled acids on crystallisation from benzene-pet. ether (60-80°) gave *αα-(3',4'-dimethyl cyclohexane)-β-aroylpropionic acids* which are entered in Table 1.

αα-(3', 4'-Dimethylcyclohexane)-γ-aryl-n-butyric acids

A solution of αα-(3', 4'-dimethylcyclohexane-β-aroylpropionic acids (3.0 g) in alcohol (25 ml) containing Pd/C (200 mg ; 10%) was treated with hydrogen (8 hrs) in a Paar apparatus at 35-40° under 35-40 lb/psi. The solution was filtered, the filtrate diluted with water, extracted with ether and the ethereal solution shaken with aqueous sodium carbonate (5% ; 4×50 ml). The alkaline extract on acidification deposited an oil which was taken up in ether, the ethereal solution dried (anhydrous $MgSO_4$) and the solvent removed. The residue depending upon its state was purified by crystallisation from benzene-petrol (60-80°) or by vacuum distillation and these reduced acids are recorded in Table 2.

2, 3-Dimethyl-8, 9-benzo and substituted 8, 9-benzo-10-keto-spiro (5,5) undecanes

Each of the above butyric acid (1.5 g) after dissolving in polyphosphoric acid (prepared from phosphorus pentoxide, 15 g and orthophosphoric acid, 10 ml) was heated in an oil bath maintained at 180-90° with occasional shaking (2 hrs). The contents were poured over crushed ice (300 g) during stirring, extracted with ether, the ethereal solution first washed with aqueous sodium hydroxide (5%) and then with water. The ethereal solution was dried (anhydrous $MgSO_4$), ether recovered and the residue on distillation gave *2, 3-dimethyl-8, 9-benzo and substituted 8, 9-benzo-10-keto-spiro (5,5) undecanes* which are given in Table 3.

TABLE 1

αα-(3', 4'-DIMETHYLCYCLOHEXANE-β-AROYLPROPIONIC ACIDS

	Aroyl	M.P. °C	Yield %	Eq. wt. (monobasic)	Mol. Formula	Analysis Found % C	H	Requires % C	H	2, 4-DNP °C
1.	Benzoyl	114	96.1	273.5	$C_{17}H_{22}O_3$	74.4	7.8	74.5	8.0	220
2.	4-Methylbenzoyl	156-7	83.9	285.8	$C_{18}H_{24}O_3$	74.9	8.2	75.0	8.3	215
3.	3, 4-Dimethylbenzoyl	107	77.7	301.6	$C_{19}H_{26}O_3$	75.5	8.7	75.5	8.6	177-8
4.	2, 4-Dimethylbenzoyl	121	71.2	301.5	,,	75.4	8.7	,,	,,	175
5.	2, 5-Dimethylbenzoyl	127	67.9	301.8	,,	75.3	8.6	,,	,,	218

αα-(3',4'-Dimethylcyclohexane)-γ-phenyl-n-butyric acid

αα-(3', 4'-Dimethylcyclohexane)-β-benzoylpropionic acid (4.0 g) was reduced by modified Clemmensen method by refluxing the contents on a sand bath for 60 hrs. On working up the reaction product in the usual manner, *αα-(3',4'-dimethylcyclohexane)-γ-phenyl-n-butyric acid* distilled at 135-6°/2-3 mm. n_D^{27} 1.5312. (Yield : 71.1%).

(Found : C, 78.5 ; H, 9.2 ; equiv., 259.7. $C_{17}H_{24}O_2$ requires C, 78.5 ; H, 9.2% ; 260.0-monobasic).

Other keto-acids on reduction by Clemmensen method gave the reduced acid in extremely poor yields but these were, however, obtained in satisfactory yields by catalytic reduction.

2, 3-Dimethyl-8, 9-benzo and substituted 8, 9-benzospiro (5, 5) undecanes

The spiro-ketone (0.8 g) was refluxed with amalgamated zinc (40 g), toluene (5 ml) glacial acetic acid (2 ml) and concentrated hydrochloric acid (60 ml) for 65-70 hrs. The reaction product on working up in the normal manner gave *2, 3-dimethyl-8, 9-benzo and substituted 8, 9-benzospiro (5,5) undecanes* (Table 4).

TABLE 2

αα-(3′, 4′-DIMETHYLCYCLOHEXANE)-γ-ARYL-*n*-BUTYRIC ACIDS

Aryl	M.P./b.p. °C	Yield %	Eq. wt. (monobasic)	Mol. formula	Analysis Found % C	H	Requires % C	H
1. Methylphenyl*	180	70.0	273.8	$C_{18}H_{26}O_2$	78.6	9.3	78.8	9.5
2. 3, 4-Dimethylphenyl	191-2/3 mm	78.4	287.5	$C_{19}H_{28}O_2$	79.0	9.6	79.2	9.7
3. 2, 4-Dimethylphenyl	165	66.4	287.7	,,	79.1	9.6	,,	,,
4. 2, 5-Dimethylphenyl	118	70.0	287.5	,,	79.0	9.6	,,	,,

* Lactone of αα-(3′, 4′-dimethylcyclohexane)-γ-hydroxy-γ-4-methylphenyl-*n*-butyric acid obtained during the Clemmensen reduction had m. p, 254-6°.
(Found : C, 79.2 ; H, 8.7. $C_{18}H_{24}O_2$ requires C, 79.4 ; H, 8.8%).
IR γ_{max}^{Nujol} 1775 cm^{-1} (lactone).

TABLE 3

2, 3-DIMETHYL-8, 9-BENZO AND SUBSTITUTED 8, 9-BENZO-10-KETO-SPIRO (5, 5) UNDECANES

Substituent in the benzene ring	b.p. °C	Yield %	Ref. index	Mol. formula	Analysis Found% C	H	Requires% C	H	2, 4 DNP °C
1. $R_1=R_2=R_3=R_4=H$	132/4 mm	71.6	$n_D^{24.5}$ 1.4987	$C_{17}H_{22}O$	84.2	9.0	84.3	9.2	195-6
2. $R_1=R_2=R_4=H$; $R_3=CH_3$	165-6/9 mm	64.2	$n_D^{24.5}$ 1.4998	$C_{18}H_{24}O$	84.3	9.1	84.4	9.4	147
3. $R_1=R_4=H$; $R_2=R_3=CH_3$	176/5 mm	64.0	n_D^{24} 1.5078	$C_{19}H_{26}O$	84.2	9.7	84.4	9.8	171
4. $R_1=R_3=H$; $R_2=R_4=CH_3$	181/7 mm	78.2	$n_D^{24.5}$ 1.5089	,,	84.3	9.5	,,	,,	176
5. $R_2=R_3=H$; $R_1=R_4=CH_3$	160/2 mm	67.6	$n_D^{24.5}$ 1.5050	,,	84.2	9.5	,,	,,	212

TABLE 4

2, 3-DIMETHYL-8, 9-BENZO AND SUBSTITUTED 8, 9-BENZO-SPIRO (5, 5) UNDECANES

Substituent in the benzene ring	b.p. °C	Yield %	Ref. index	Mol. formula	Analysis Found % C	H	Requires % C	H
1. $R_1=R_2=R_3=R_4=H$	95-6/2 mm	53.1	$n_D^{28.5}$ 1.4875	$C_{17}H_{24}$	89.4	10.3	89.5	10.5
2. $R_1=R_2=R_4=H$; $R_3=CH_3$	162/10 mm	66.1	n_D^{29} 1.5035	$C_{18}H_{26}$	89.1	10.6	89.3	10.7
3. $R_1=R_4=H$; $R_2=R_3=CH_3$	165/4 mm	46.0	n_D^{24} 1.5350	$C_{19}H_{28}$	89.0	10.7	89.1	10.9
4. $R_1=R_3=H$; $R_2=R_4=CH_3$	185/8 mm	60.2	n_D^{28} 1.5401	,,	89.0	10.8	,,	,,
5. $R_2=R_3=H$; $R_1=R_4=CH_3$	179/3 mm	60.0	n_D^{22} 1.5521	,,	89.1	10.7	,,	,,

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NOTES

Equilibrium Studies of the Magnesium-Hydrogen System in Mixed Solvents

E.A. HASSAN, M.F. EL-HADI and N.A. BADAWY

Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt.

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SELECTIVITY coefficients have been measured at 25° for $Mg^{++}-H^{+}$ system using Zeo-Karb 225 cation exchange. Methanol-water, ethanol-water and isopropanol-water mixtures were used at external solution concentration of 10, 20 and 30% (V/V). The total ionic strength of the medium was maintained at both 0.025 and 0.1*M*. If other conditions are comparable, the order of the selectivity coefficients in alcohol-water system is: isopropyl>ethyl>methyl alcohol. The uptake of each solvent mixture by both pure hydrogen resinate and pure magnesium resinate was determined. ΔF^{*} for each reaction was calculated.

Although many results of ion-exchange experiments in aqueous media have been published, there are very few literature references to ion-exchange in nonaqueous media or in mixed solvents. These studies revealed the role of the solvent on the ion-exchange process. The purpose of the present work was to compare ion-exchange equilibria of one pair of ions in nonaqueous media with those in aqueous media and to ascertain whether there was a relationship between these equilibria and the swelling of the resin.

Experimental

The ion-exchange resin Zeo-Karb 225 was sieved between 250-420 microns, that fraction which was used for all the experiments. The resin was subjected to hydrogen-sodium twice by treatment with 2*M* sodium chloride and 3*N* hydrochloric acid,

All the chemicals used were either of E. Merck GR or BDH Analar grade.

Equilibrium procedure: The experimental procedures for the equilibrium studies were identical with those used for similar studies in aqueous media[1].

Solvent uptake—The uptake of each solvent mixture by both pure hydrogen[2] resinate and pure magnesium resinate was determined experimentally. The concentration of magnesium ion was determined titrimetrically with EDTA. The concentration of hydrogen ions was determined by titration against standard alkali.

Results and Discussion

The slectivity coefficient, K, is calculated for each exchange reaction from the equation

$$K = \frac{(mH^{+})^{2}}{mMg^{2+}} \times \frac{\bar{N}Mg^{2+}}{(\bar{N}H^{+})^{2}}$$

From the plots of equilibrium quotient vs. resin composition, it may be noted that at total ionic strength of 0.025*M* in pure aqueous solution, the selectivity coefficient values were always lower than unity all over the whole range of equivalent fraction, indicating that the resin is more selective to hydrogen ions than magnesium ions. On the other hand, as the methyl alcohol partially replaced the aqueous solution, such reversal in selectivity has disappeared and the affinity of the resin to magnesium ions is enhanced.

Such affinity is greatly increased by increasing the proportion of the alcohol, thus reaching its maximum value at 30% (V/V). As the ionic strength of the medium is increased up to 0.1*M*, the selectivity curves exhibited a similar behaviour, but to a slightly greater extent. At such concentration, there are two factors contributing together for the enhancement of the affinity of the resin to magnesium ions, one such factor is the increase in the ionic strength of the external solution, the other factor is the partial displacement of the pure aqueous solution by alcohol. In ethanolic solution when the ionic strength is maintained at 0.025*M*, the same effect on the selectivity coefficient has been obtained. The most interesting feature of the obtained curves is the close similarity in shape to that already found in methanolic solution at the same ionic strength, the only difference is that the present curves showed a slightly greater affinity of the resin for the studied cation. When the same proportions of ethanol were used at total ionic strength of 0.1*M*, a selectivity curve of much greater similarity to those previously obtained in methanolic solution, except that the 30% (V/V) curve exhibits a sharp maximum. Studying the effect of isopropanol on the selectivity of the resin, using the same three proportions of the solvent. maintaining the constant ionic strength at 0.025*M*, results in an affinity curve of great similarity to the corresponding curves in presence of either methanol or ethanol. A greater variation in the selectivity curves has been obtained

at total ionic strength of 0.1*M*, the selectivity coefficient reaches its maximum value e. g ; K=36 at $N_{Mg^{++}}$ of 0.9, such value cannot be obtained in the presence of another two solvents.

It may be noted, therefore, that all the selectivity curves agreed well with the fact that there is an overall increase in the affinity of the resin towards magnesium ions, when organic solvent was added, and such affinity is further increased by increasing the proportion of the solvent employed. The presence of some organic solvent reduces the swollen volume of magnesium resinate, a fact which cannot be obtained for hydrogen resinate ; the possibility of a relationship between swelling and selectivity is indicated. The increase in selectivity may be due in part to increase in the activity coefficient ratio f_{HRes}/f_{MgRes} caused by an increase in the concentration of the resin phase. A similar effect is observed in aqueous media in which the ionic strength of the external solution is increased from 0.025 to 0.1*M*, thereby reducing the swollen volume of the resin[8]. The exchange data in methanol-water, ethanol-water and isopropanol-water mixtures reflect a greater selectivity of the ion-exchange resin for the metallic magnesium in the above solvent mixtures than in pure water.

In the above studied water alcohol mixtures, log k is seen in the figure to vary essentially linearly with 1/D as represented by other investigators[4-7] for ion exchange in mixtures of water and another polar solvent ; this proves that under the conditions studied, electrostatic ion interaction rather than changes in the ion solvation.

Oiwa's empirical treatment lends weight to the interpretation of the maximum as primarily a medium effect involving the proton and operative in both the resin and external phases. Due to the close similarity between methanol and ethanol, the selectivity maximum was observed in ethanol-water mixtures as well as in methanol-water mixtures. The maximum in the selectivity curve that was already found in ethanol-water mixtures was of higher magnitudes, than that in methanol-water mixtures, but it is proved to be located at higher values of equivalent fraction of the magnesium ion in the resin phase. It has been observed that, the selectivity maximum in isopropanol-water mixture will be significantly higher than those predicted in the presence of ethanol. The sharpness in the maximum has been increased by gradually increasing the proportion of alcohol to water up to 30% (V/V) alcohol ; such phenomenon support the fact that the proton effect is remarkable by increasing the percentage of the added solvent. On the other hand, using 30% isopropanol at total ionic strength of 0.025*M*, no such maximum has been observed.

The free energy of activation was calculated for this exchange for each of the solvent compounds. It may be noted, however, that as the negativity of ΔF^* increases[8], the tendency of the exchange reaction to proceed from the hydrogen form of the resin to the magnesium form increases.

There are two points of particular interest in this exchange system. First, the amount of the solvent taken up by the resin decreased as long as it was converted to the magnesium form as can be seen in the table by comparing the values of solvent uptake at one and the same solvent composition and definite ionic strength. Secondly, it has been found that the order of solvent uptake, if other conditions are comparable, for both hydrogen and magnesium resinates is methyl>ethyl>isopropyl alcohol, which is exactly the reverse of the order of selectivity coefficients under the same conditions, Thus it may be noted, however, that the increase in the total ionic strength of the external solution has the same influence at that of the organic solvent on , the selectivity coefficient.

TABLE—SOLVENT UPTAKE BY BOTH HYDROGEN AND MAGNESIUM RESINATES AT VARYING IONIC STRENGTHS AND SOLVENT COMPOSITION

Total ionic strength	Type of solvent	Solvent composition % of alcohol (V/V)	Solvent/lg resin	
			H resinate	Mg resinate
0.025	methanol-water	10	0.652	0.532
		20	0.584	0.480
		30	0.494	0.420
0.1		10	0.538	0.509
		20	0.502	0.488
		30	0.489	0.408
0.025	ethanol-water	10	0.500	0.482
		20	0.462	0 480
		30	0.402	0.379
0.1		10	0.475	0.421
		20	0.400	0.378
		30	0.382	0.320
0.025	isopropanol-water	10	0.427	0.400
		20	0.389	0.366
		30	0.362	0.292
0.1		10	0.372	0.320
		20	0.356	0.282
		30	0.302	0.256

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Manganese(III) Complexes of Salicylidene Amino Acids

R. L. DUTTA and R. K. RAY

Department of Chemistry, The University of Burdwan, Burdwan 713104, West Bengal.

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A number of manganese(III) complexes are known but there is no report yet on a bis(ligand) manganese(III) complex of a tridentate dibasic Schiff base[1-4].

We report here the synthesis of alkali/alkaline earth metal salts of the hitherto unknown bis (salicylideneglycinato) manganese(III) (salglyH$_2$ = salicylideneglycine) and related complexes by refluxing a mixture of manganese(II) acetate, salicylaldehyde and glycine in aqueous ethanol in presence of a large excess of an alkali/alkaline earth acetate (Method A). A dimeric tetraaquo μ-bis (salicylideneglycinato) dimanganese(II), [Mn(salgly) (H$_2$O)$_2$]$_2$, is also readily oxidised in aqueous ethanol in presence of added glycine, salicylaldehyde and alkali/alkaline earth acetates (Method B). In the absence of alkali/alkaline earth acetate in Method A only the dimeric manganese(II) complex crystallises while in Method B the insoluble dimeric complex remains unchanged. Potassium salt of bis(5,6-benzosalicylidene α-alaninato) manganese(III) complex could be easily obtained following both Methods A and B using α-alanine and 2-hydroxy-1-naphthaldehyde. However by refluxing manganese (II) acetate, salicylaldehyde and α-alanine, (β-alanine, valine or leucine) in presence of excess Na/K/Ca acetates a clear brown-red solution was obtained as usual but no compound could be crystallised.

Na[Mn(salgly)$_2$] is a uni-univalent electrolyte in methanol ($\Lambda_M \sim 70$ ohms^{-1}cm^2 mole^{-1}). The compound liberates one equivalent of iodine from acidified KI. The $\nu_{C=N}$ and ν_{COO^-} stretches appear as strong bands around 1590 cm^{-1} and 1638 cm^{-1} respectively while the aromatic $\nu_{C=C}$ appears[5,6] at 1545 cm^{-1}. The magnetic moments of this and related complexes (Table 1) are in the range 4.75-4.90 B.M. indicating their high spin $t_{2g}^3\ e_g^1$ distribution. The expected electronic transitions, unfortunately, could not be identified due to poor resolution. These compounds are the first ever examples of anionic Schiff base complexes of manganese(III). A dimeric manganese(II) complex is utilised, for the first time, as the starting material for the synthesis of a manganese(III) complex.

Experimental

[Mn(salgly) (H$_2$O)$_2$]$_2$ was obtained by following published procedure[7].

Synthesis of K [Mn(salgly)$_2$] 4H$_2$O :

Method A : A hot solution of glycine (0.3 gm in 5 ml water) was added to a hot solution of salicylaldehyde (0.5 gm in 10 ml ethanol) and the mixture was refluxed for 30 mins. To this potassium acetate (3 gm in 10 ml ethanol) was added and again refluxed for 30 mins. Manganese (II) acetate tetrahydrate (0.5 gm in 10 ml ethanol) was added to the above solution and the whole solution was further refluxed for 2 hrs. The solution was then filtered and the dark brown filtrate was left in a refrigerator overnight. Beautiful shining chocolate coloured crystals were filtered, washed with ice cold alcohol and dried over silica gel.

Method B : An aqueous solution of glycine (0.3 gm in 5 ml water) was added to salicylaldehyde (0.5 gm in 10 ml ethanol) and refluxed for 30 mins. Potassium acetate (7 gm) and ethanol (10 ml) were then added and refluxed for 30 mins. To the above solution was added yellow coloured [Mn(salgly) (H$_2$O)$_2$]$_2$ (1 gm) and the mixture refluxed for 1 hr. to provide a dark brown solution. The solution was manipulated as in Method A.

The compound is soluble in methanol, ethanol, pyridine, dimethylsulfoxide, etc, For the synthesis

TABLE 1. CHARACTERISATION DATA OF MANGANESE (III) COMPLEXES OF SALICYLIDENE AMINO ACIDS

Complex (colour and magnetic moment)	Method of Synthesis	% Mn	% Total metal	% N	% C	% H	% H$_2$O
Na[Mn(salgly)$_2$]3H$_2$O	A	Found : 11.2	16.0	5.8	44.5	4.0	11.2
(Chocolate ; μ=4.75 B. M.)	B	Found : 11.1	16.0	5.8	44.3	4.1	11.0
		Calc. : 11.3	16.0	5.7	44	4.1	11.1
K[Mn(salgly$_2$]4H$_2$O	A	Found : 10.6	18.1	5.2	4.	4.0	13.0
(Chocolate ; μ=4.82 B. M.)	B	Found : 10.5	17.9	5.4	41.0	4.0	13.1
		Calc. : 10.5	18.0	5.3	41.4	4.0	13.8
Ca[Mn(salgly)$_2$]CH$_3$COO . 3H$_2$O	A	Found : 9.8	17.0	5.1	43.0	4.0	9.6
(Chocolate ; μ=4.80 B. M.)		Calc. : 9.7	16.9	4.9	42.7	4.0	9.6
K[Mn(5, 6-benzosal α-alan)$_2$]2H$_2$O	A	Found : —	15.2	4.5	54.4	4.3	5.8
(Chocolate ; μ=4.91 B. M.)		Calc. : —	15.3	4.5	54.9	4.2	5.8

salglyH$_2$ = salicylideneglycine ; 5, 6-benzosal α-alanH$_2$ = 5, 6-benzosalicylidene α-alanine.

of sodium and calcium salts, sodium acetate and calcium acetate were used in place of potassium acetate.

Analyses and Measurements: Manganese(III) content of salicylideneglycine complex was determined iodometrically. Total metal percentage was estimated by igniting the complexes and converting to sulphates. Nitrogen was estimated by Duma's method. C,H analyses were done at CDRI, Lucknow. Magnetic susceptibilities were obtained using the Gouy technique with $CuSO_4 \cdot 5H_2O$ as calibrant. IR spectra were run as KBr matrices.

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Kinetics and Mechanism of Osmium(VIII) Catalysed Oxidation of Dimethyl Sulphoxide with Potassium Hexacyanoferrate(III) in Aqueous Alkaline Medium

P. S. RADHAKRISHNA MURTI & S. C. PADHI

Department of Chemistry, Berhampur University, Berhampur-760007. (Ganjam), Orissa.

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THE reaction DMSO – Mn^{3+} has been employed as a red-ox initiator for vinyl-polymerisation.[1] We have recently reported a kinetic study of DMSO-oxidation by Cr(VI) and Ce(IV)[2]. Recently we have communicated the kinetics of oxidation of DMSO by chloramine-T(CAT) in acid medium and OsO_4 catalysed oxidation of DMSO by CAT in alkaline medium[3]. This present communication concerns with the oxidation of DMSO by potassium hexacyanoferrate(III) in alkaline medium catalysed by OsO_4.

Materials and Methods :

E. Merck (G. R. grade) sample of potassium hexacyanoferrate(III), sodium carbonate free sodium hydroxide, potassium chloride (BDH) AR grade and dimethyl sulphoxide (BDH) AR grade were employed. Osmium(VIII) solution was prepared from Osmium tetroxide. Aqueous solution of potassium hexacyanoferrate(III) was stored in dark amber coloured bottles to avoid photochemical reaction. The ionic strength was kept constant throughout the study by using 0.025 *M* KCl. The rate constants have been computed by the usual tangential method and are reproducible within 3% error.

Results and Discussion

The reaction was found to be first order in the substrate and first order in ferricyanide. The first order rate constant increases with increasing concentration of DMSO up to a limiting concentration 0.035 *M* of DMSO. Beyond this concentration, k_1 remains constant indicating zero order with respect to DMSO (Table 1).

TABLE 1

EFFECT OF VARYING SUBSTRATE CONCENTRATION

Ferricyanide = 0.00125 *M*, NaOH = 0.0025 *M*, KCl = 0.025 *M*, $OsO_4 = 3.9 \times 10^{-6}$ *M*, Substrate = DMSO. Temp. 35°C.

[Substrate] *M*	k_1 sec^{-1}
0.00205	0.0001636
0.00402	0.000331
0.00717	0.0005155
0.035	0.001395
0.070	0.001727
0.140	0.001727
0.210	0.001727

In the concentration range where the order with respect to DMSO is zero it was decided to vary the ferricyanide concentration. Though it is expected that the first order rate constant should remain constant with increasing $[Fe(CN)_6^{3-}]$ to prove the first order nature with respect to ferricyanide, there is a decrease in the rate constant. This apparent decrease in rate may be attributed to the mass law effect. As the reaction product ferrocyanide is formed, it shifts the equilibrium towards ferricyanide and hence the observed retarding rate. This has been independently checked by performing a run with 0.00125 *M* of potassium ferrocyanide, where there was no reaction at all, confirming our reasoning that the observed retardation with increasing ferricyanide is only due to the mass law effect (Table 2).

TABLE 2

EFFECT OF VARYING FERRICYANIDE CONCENTRATION

NaOH=0.0025 *M*, DMSO=0.07 *M*, KCl=0.025 *M*, OsO_4=3.9×10^{-6} *M*. Temp. 35°C.

[Ferricyanide] *M*	k_1 sec^{-1}
0.00125	0.001727
0.002	0.001394
0.003	0.0009892
0.004	0.0007968

Variation of alkali and Osmium (VIII) :

The order with respect to Osmium(VIII) is one, The first order rate constant increases with increasing concentration of Os(VIII). The order with respect to alkali is also unity. The rate constants at different concentrations of Os(VIII) and NaOH are reported in Tables 3 and 4.

TABLE 3

EFFECT OF VARYING ALKALI

Ferricyanide=0.00125 *M*, KCl=0.025 *M*, OsO_4=3.9×10^{-6} *M*, DMSO=0.002 *M*. Temp. 35°C.

[NaOH] *M*	k_1 sec^{-1}
0.0025	0.0001636
0.005	0.000549
0.0075	0.000620
0.01	0.000752

TABLE 4

EFFECT OF VARYING Os(VIII)

DMSO=0.07 *M*, NaOH=0.0025 *M*, KCl=0.025 *M*, Ferricyanide=0.00125 *M*, Temp. 35°C

[Os(VIII)]×10^6 *M*	k_1 sec^{-1}
3.12	0.001189
3.9	0.0017
5.85	0.00239
7.8	0.00376

The variation of ionic strength was studied by varying the concentration of KCl. Increasing concentration of KCl increased the rate. Effect of KBr is same as KCl. But KI enhances the rate slightly (Table 5).

TABLE 5

EFFECT OF VARYING IONIC STRENGTH

NaOH=0.0025 *M*, OsO_4=3.9×10^{-6} *M*, DMSO=0.002 *M*, Ferricyanide=0.00125 *M*. Temp. 35°C

Salt	Concⁿ. *M*	k_1 sec^{-1}
	0.025	0.000163
	0.05	0.000219
KCl	0.075	0.000267
	0.1	0.000292
KBr	0.025	0.0001498
KI	0.025	0.000198

It is pertinent to point out here that the reaction between DMSO and Ferricyanide in the *p*H range 6.85 to 9.4 does not take place.

Mechanism :

In accordance with the observed experimental data it is possible to postulate the following mechanism for substrate concentrations at and below 0.035 *M*.

$$OsO_4(OH)_2^{2-}+OH^- \xrightleftharpoons{\text{fast}} OsO_4(OH)_3^{3-}$$

$$Fe(CN)_6^{3-}+OsO_4(OH)_3^{3-} \xrightleftharpoons{\text{slow}} \text{complex}$$

$$\text{Complex}+DMSO \xrightarrow{\text{slow}} \text{Products.}$$

The above mechanism clearly explains the first order dependence on substrate, Ferricyanide, [OH^-] and Os(VIII). Such unit dependence on substrate, oxidant, alkali and catalyst was earlier observed in Se(IV) oxidations[4] involving the formation of Se(V) as an intermediate in the reversible rate determining step followed by its fast oxidation to Se(VI) by Os(VIII) ; the catalyst being generated in a subsequent fast oxidation of Os(VII) by hexacyanoferrate(III).

In the concentration range above 0.035 *M* of the substrate the order with respect to alkali and hexacyanoferrate(III) is each one but the order with respect to substrate is zero. This can be visualised by the mechanism

$$OsO_4(OH)_2^{2-}+OH^- \xrightleftharpoons{\text{fast}} OsO_4(OH)_3^{3-}$$

$$Fe(CN)_6^{3-}+OsO_4(OH)_3^{3-} \xrightleftharpoons{\text{slow}} \text{Complex.}$$

$$\text{Complex}+DMSO \xrightarrow{\text{fast}} \text{Products.}$$

The above mechanism suggests a possible complex formation between hexacyanoferrate(III) and Os(VIII). Formation of such complex has also been postulated previously by Mushran[5] and Muralikrishna[6].

In accordance with the mechanism the rate law at high concentrations of the substrate takes the form

$$-d[Fe(CN)_6^{3-}]/dt=k[Fe(CN)_6^{3-}][OH^-][Os(VIII)]$$

and at lower concentrations of the substrate the rate law becomes

$$-d[Fe(CN)_6^{3-}]/dt=k\ (S)\ [Fe(CN)_6^{3-}]\ [OH^-]\ [Os(VIII)]$$

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Studies on Azido Complexes of Cobalt : Part I

S. K. CHATTERJEE, P. K. DAS

Department of Chemistry, Hooghly Mohsin College, Chinsura, Hooghly, West Bengal

and

S. K. BOSE

Department of Chemistry, University College of Science, Calcutta-700 009

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ONLY a few transition metal ions are known to form azido complexes. It is only with cobalt as the central metal atom do we have a variety of complexes of the type MA_5B^1, $MA_4B^2_2$, $M(AA)_2B_2$ and $MA_3B^3_3$ where A is a unidentate group such as ammonia, AA is a bidentate group such as ethylenediamine[4], 1, 10 orthophenanthroline[5], 2 2' bipyridyl[6], acetylacetone[7], and B is the azido group.

Of the bidentate ligands notable exceptions are dimethylglyoxime and biguanide. The synthesis of azido complexes of cobalt with dimethylglyoxime has been reported recently[8]. In this communication we report the preparation and characterisation of the pair cis and trans diazido bis biguanide cobalt(III) azide.

Experimental

Trans $Co[(big\ H)_2(N_3)_2]N_3 \cdot H_2O$ was prepared by reacting a saturated solution of trans$[Co(big\ H)_2Cl_2]Cl$[9] with an excess of solid sodium azide in a water bath kept at 60°-80° for half an hour. The solution is cooled and kept in a refrigerator overnight when orange crystals separate out. The crystals are filtered, washed with rectified spirit ; the product is then recrystallised from water and dried in air.

The starting meterial for the preparation of cis$[Co(big\ H)_2(N_3)_2]N_3.H_2O$ is cis$[Co(big\ H)_2(NH_3)_2]Cl_3$ which was prepared by the method of Dutta & Sircar[10]. The compound was suspended in water air was passed through it for several hours and warmed on a water bath at 60°-80° for about an hour, and then treated with excess of solid sodium azide for half an hour at 60°-80°. The resulting solution was left in refrigerator over night and filtered to collect the violet crystals. The crystals were washed with water and alcohol and recrystallised from water and then air dried.

Cobalt was determined by converting it to cobalt sulphate and weighing as anhydrous cobalt sulphate. Total nitrogen was estimated by Duma's Method. Labile azide which constitutes one-third of the total azide was estimated by precipitating as silver azide and weighing. Analytical data are given in Table 1.

TABLE 1

CHEMICAL ANALYSIS OF THE COMPLEXES

Compound	Co	N	N_3^-	
Trans$[Co(big\ H^+)_2(N_3)_2]N_3, H_2O$	14.54	65.69	10.87	% Calcd.
	14.10	64.80	9.80	% Found.
Cis$[Co(big\ H^+)_2(N_3)_2]N_3, H_2O$	14.54	65.09	10.37	% Calcd.
	14.00	66.00	10.57	% Found.

Results and Discussion

The visible and U. V spectra was determined in a Beckman Spectrophotometer Model D. U. In aqueous media the cis compound has two peaks at 296 nm ($\epsilon_M = 316$) and 508 nm ($\epsilon_M = 168$). The trans compound has also two bands at 350 nm ($\epsilon_M = 208$) and at 482 nm ($\epsilon_M = 208$). For both compounds there is no evidence of any splitting of the bands in the visible region.

The i.r. spectra were recorded in a Beckman I.R. 20 in KBR pellets.

The bending mode $\delta(N_3)$ and the asymmetric stretch of co-ordinated azides $\nu(N_3)$ as lie in the regions 626-677 cm^{-1} and 2037-2092 cm^{-1} respectively for azide cobaltamine complexes[4]. The symmetric $\nu(N_3)$ S stretch[11], when it is observed as in $MoCl_4(N_3)_2$, occurs in the region 1190-1260 cm^{-1}.

On the basis of these the following assignments if i.r. bands may be made and is given in Table 2 in which v.s (denotes very strong, S means strong) and m indicates medium.

The assignment of $\nu(N_3)$ S is doubtful as a band at 1255 (m) is also observed in $[Co(big\ H)_2OH.H_2O]SO_4$, 2.5 H_2O.

TABLE 2

INFRA-RED SPECTRA

	Trans	Cis
$\nu(N_3)$ as	2050 (v.s.)	2015 (v.s)
$\nu(N_3)$ S	1245 (s)	1280 (s), 1285 (s)
$\delta(N_3)$	650 (m)	610 (m)

The vibration of lattice water are generally found in the region (3550-3200) cm^{-1} corresponding to the symmetric and antisymmetric O-H stretching modes[12]. In both these azido complexes strong bands appear in these regions viz. 3200, 3300 and 3400 cm^{-1} for trans and a very broad strong absorption band from 3100 to 3400 cm^{-1} for the cis. An absorption at 1670 (S) for trans and 1680 (S) for cis may be assigned to H–O–H bending mode[12].

The azide outside the co-ordinating sphere for both these compounds was precipitated with silver nitrate, the filtrate acidified with perchloric acid, and then irradiated. It is found that in contrast to azido complexes containing ammonia and ethylenediamine, these biguanide complexes are rather inert to irradiation with visible light in perchloric acid medium and undergo decomposition on prolonged irradiation with ultra-violet light (365 nm). The details of this photodecomposition are under investigation.

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Titrimetric Determination of Lead(II), Molybdate and Phosphate using Pyridinol-Azo-Dyes as Visual Indicators

J. P. GUPTA, B. S. GARG and R. P. SINGH

Department of Chemistry, University of Delhi, Delhi-110007(India).

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IN the present study pyridinol azo dyes 1-(2,3-dihydroxy-4-pyridylazo)-4-benzene sulphonic acid (DHP-4S) and 1-(5-chloro-4-pyridylazo-2,3-diol)-4-benzene sulphonic acid (CPD-4S) have been successfully used as indicators for the titrimetric determination of lead (II)(complexometrically) and molybdate, phosphate (volumetrically). Earlier, formation of these dyes have been used as a sensitive test for the detection and determination of nitrite[1]. The dyes have also been utilised for the complexometric determination of Zn(II), Cd(II) and Hg(II)[2].

Experimental

Reagents

Standard lead(II), molybdate and phosphate solutions were prepared by dissolving appropriate amounts of Analar $Pb(NO_3)_2$, $Na_2(MoO_4)$. $2H_2O$ and KH_2PO_4 respectively in double distilled water. 0.1% Dye solutions were prepared in doubly distilled water.

Recommended Procedure

Determination of Lead(II) : To a suitable aliquot containing 10.35-414.4 mg of lead(II) add 5 ml of NH_4Cl/NH_4OH buffer of suitable pH (Table 1) and 0.1-0.3 ml of 0.1% indicator solution (DHP-4S or CPD-4S). Dilute the solution to approximately 20 ml by adding doubly distilled water and titrate at room temperature (27°) against standard EDTA ($1\times10^{-1}M$) taken in a microburette till a sharp colour change (magenta or red to orange) is obtained (Table 1). A white precipitate formed during the titration disappears on shaking. Titrations in reverse order can also be performed but the buffer should be added a few millilitre before the end-point.

TABLE 1

OPTIMUM CONDITIONS FOR THE TITRATION OF LEAD(II), MOLYBDATE AND PHOSPHATE

Variables	Titration of Lead (II)		Titration of molybdate		Titration of phosphate
	DHP-4S	OPD 4S	DHP-4S	OPD-4S	OPD-4S
Colour change at the end-point	Red to Orange	Magenta to Orange	Orange to Red	Orange to Magenta	Orange to Magenta
Temperature range	15-30°C	15-30°C	30-60°C	30-60°C	20-60°C
Indicator concentration 0.1%	0.1-0.3 ml	0.1-0.3 ml	0.1-0.4 ml	0.1-0.4 ml	0.1-0.4 ml
pH range, buffer	8.0-10.0 NH_4Cl/NH_4OH	8.0-10.5 NH_4Cl/NH_4OH	5.5-7.0 Pyridine buffor	5.5-7.0 Pyridine buffer	5.5-7.0 Pyridine buffer
Standard deviation	0.013	0.011	0.014	0.018	0.018
% Relative Error	0.17%	0.17%	0.25%	0.40%	0.40%
pH at which titrations performed	10.0	10.0	7.0	7.0	7.0

Determination of Molybdate and Phosphate : To a suitable aliquot containing 1.60-160.0 mg of molybdate or 0.95-76.0 mg of phosphate, add 5 ml of pyridine buffer of suitable pH (Table 1) and 0.1 to 0.4 ml of 0.1% indicator solution (Table 1). Dilute the solution to approximately 20 ml and titrate the contents at 30° with shaking, against standard $Pb(NO_3)_2$ (1×10^{-1} *M*) until the end-point is reached. Reverse titrations have also been performed.

Titrations in presence of diverse ions

Interferences due to a large number of foreign ions have been studied by taking 82.88 mg of lead (II), 64.00 mg of molybdate or 28.50 mg of phosphate and following the recommended procedure as given above. Masking agents were also used to undo some of the interferences. The results of the studies are summarised below :

Titration of Lead(II)

Ions like F^-, Cl^-, Br, I^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, CH_3COO^-, ClO_4^-, BO_3^{3-}, CNS^-, thiourea, NO_3^-, Tl^+ and Sr^{2+} do not interfere when present up to 5000 ppm level. However, PO_4^{3-} interferes even in traces. The following ions do not interfere (amounts in ppm). Masking agents, wherever used are given in brackets.

S^{2-}(100-200), tartarate (100-200), citrate(200), Ti^{4+}(120) Sb^{3+}(122), MoO_4^{2-}(24-48), Ge^{4+}(100) (F^-), WO_4^{2-}(184), UO_2^{2+}(240), Ia^{3+}(70), In^{3+}(23), Os^{8+}(5) (CN^-), V^{5+}(25.5), Sn^{2+}(25) (F'), Rh^{3+}(4.1), Hg^{2+}(5000) (CN^-), Cu^{2+}(5000) (CN^-), Co^{2+}(1000) (CN^-), Ni^{2+}(1500) (CN^-), Zn^{2+}(654) (CN^-), Fe^{2+} (280) (CN^-) and Cd^{2+}(112.4) (CN^-).

Titration of Molybdate and Phosphate

Anions like CH_3COO^-, ClO_4^-, BO_3^{3-}, CNS^-, thiourea, NO_3^- and I^- do not interfere up to 5000 ppm level. However, F^-, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_8^{2-}$, S^{2-}, $C_4H_4O_6^{2-}$, citrate, $C_2O_4^{2-}$, Cu^{2+} and Cd^{2+} interfere seriously in both the cases.

For molybdate the tolerance limits (in ppm) of various ions are given below. Masking agents. if used, are mentioned in parentheses.

Cl^-(1000), Br^-(1000), CN^-(500), Ti^{4+}(6), Sb^{3+} (30.5), Sr^{2+}(11-22), Fe^{3+}(5), WO_4^{2-}(18.4-46), Tl^+(5.1), UO_2^{2+}(136), La^{3+}(7), Os^{8+}(4.8), V^{5+}(10), Sn^{2+} (50 – 100), Rh^{3+}(8.2) and Hg^{2+}(10-20) (I^-).

For phosphate the tolerance limits of various ions, with masking, given below :

Ti^{4+}(12), Sb^{3+}(30.5), Sr^{2+}(4.5), Ge^{4+}(10), WO_4^{2-} (184), Tl^+(20.5), UO_2^{2+}(68), La^{3+}(14), In^{3+}(46) Os^{8+} (9.7), V^{5+}(25.5), Sn^{2+}(5), Rh^{3+}(16.5), Hg^{2+}(1000) (CN^-), Co^{2+}(15) (CN^-), Ni^{2+}(58) (CN^-), Zn^{2+}(65.4) (CN^-) and Fe^{2+}(5.6) (CN^-).

Results and Discussion

Optimum conditions for the estimation of lead(II) molybdate and phosphate have been established and statistical evaluation of the results have been carried out (Table 1).

In molybdate titrations, lead to molybdate ratio at the equivalence point is 1 : 1 which corresponds to the formation of $PbMoO_4$ and in phosphate titrations the ratio of lead to phosphate in the precipitate is 5 : 3 corresponding to an apatite type phosphate[3-4] $Pb_5(PO_4)_3OH$.

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Separation of Germanium from Arsenic by Paper Chromatography

J. SUBRAHMANYAM and M. N. SASTRI*

Department of Chemistry, Andhra University, Waltair-530 003.

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LEDERER[1] was able to separate germanium from Arsenic and other elements by paper chromatography using *n*-butanol saturated with N HCl using the ascending technique. The R_f values were Ge(IV), 0.26; As(V), 0.84; and As(III) 0.52. Ladenbauer and Hecht[2] made use of alcohols mixed with HNO_3 as solvents in the paper chromatographic separation of germanium by the descending technique.

In this communication we report our studies on the paper chromatographic separation of these two elements using ketones and ether solvent systems. Each solvent was studied in the three acid media-hydrochloric, hydrobromic and nitric acid.

Experimental

The descending technique was employed for the separations. Whatman No. 1 'Chromatographic quality' filter paper was used as the inert support. The strips were of the size 8×45 cm.

Chemicals and Reagents

Germanium dioxide sample was of the purest quality supplied by Fairmount Chemical Company, New York. The arsenious oxide and sodium arsenate were 'pro analyse' grade samples supplied by E. Merck.

The germanium solution (0.06%) was prepared by weighing the requisite quantity of germanium dioxide and mixing with 0.5 gm. of sodium carbonate and 25 ml of water. The sodium germanate thus obtained was neutralised with sufficient hydrochloric acid and diluted to 100 ml.

1% solutions of As(III) and As(V) were similarly prepared.

A 0.05% solution of phenyl fluorone in a mixture of ethyl alcohol and dilute sulphuric acid (75 : 25) was used as a spraying reagent for the identification of Ge(IV).

The yellow spot obtained when the paper strip was exposed to hydrogen sulphide identified As(III).

As(V) was identified by the benzidine-potassium iodide reagent spray which is prepared as follows: 0.1 gm. of benzidine and 0.1 gm. of potassium iodide were dissolved in 10 ml of 3 N HCl and the solution was filtered. The solution when sprayed identified the As(V) as a dark brown spot.

The solvents acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) were of laboratory reagent quality and purified freshly before use according to the standard procedures.

Results

The following Table summarises the R_f values with solvent systems of varying compositions :

Sl. No	Solvent system (vol. %)			R_f values		
				Ge (IV)	As (III)	As(V)
1.	Acetone	(90%)+HCl	(10%)	0.95	0.72	0.85
2.	Acetone	(90%)+HNO_3	(10%)	0.30	0.12	0.65
3.	Acetone	(90%)+HBr	(10%)	0.68	0.50	0.86
4.	MEK	(90%)+HCl	(10%)	0.82	0.81	0.69
5.	MEK	(90%)+HNO_3	(10%)	0.16	0.12	0.42
6.	MEK	(90%)+HBr	(10%)	0.28	0.35	0.50
7.	MIBK	(90%)+HCl	(10%)	0.59	0.48	0.11
8.	MIBK*	(90%)+HNO_3	(10%)	0.10	0.10	0.13
9.	MIBK*	(90%)+HBr	(10%)	0.43	0.48	0.40
10.	Dioxane	(90%)+HCl	(10%)	0.74	0.70	0.21
11.	Dioxane	(90%)+HNO_3	(10%)	0.40	0.83	0.73
12.	Dioxane	(90%)+HBr	(10%)	0.11	0.10	0

* Two layers formed and the upper layer was taken.

It can be seen that in all the cases the R_f values for Ge(IV) and As(III) are close, while the values for Ge(IV) and As(V) are wide enough to be amenable for separation. As(III) was therefore converted to As(V) by the addition of small quantities of hydrogen peroxide before running the chromatogram. This pretreatment gave very satisfactory separation of the two elements with the solvent systems 2, 5, 7, 10 and 11. Further, the separation time is of the order of 6-8 hours as compared to 22-24 hours with butanol-HCl/HNO_3 systems recommended by Lederer and Ladenbauer.

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β-Resorcylaldehyde as a Reagent for the Spectrophotometric Determination of Ferric Ions

B. M. DESAI and (Miss) J. V. PARGHI

Chemistry Department, M.G. Science Institute, Ahmedabad-380 009

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WHILE a number of phenolic carbonyl compounds have been investigated as reagents for the spectrophotometric determination of ferric ions, β-resorcylaldehyde has not been investigated so far for this purpose. The present article reports the use of β-resorcylaldehyde as reagent for the spectrophotometric determination of ferric ions.

Experimental

β-Resorcylaldehyde : 0.005 *M* solution was prepared in 40% ethyl alcohol.

TABLE 1

DETERMINATION OF FERRIC IONS IN DRUGS BY COLORIMETRIC METHOD USING β-RESORCYLALDEHYDE AS REAGENT

pH : 2.5 λ max. = 450 nm

Drugs	Manufacturing Company	Iron expected	Absorbance of ferric β-resorcyl-aldehyde complex	Iron calculated from absorbance
Polycytol tablet	Alembic Chemicals	Dried $FeSO_4$ 0.195 g.	0.140	0.191 g.
Iberol tablet	Abbott Laboratories Private Ltd.	$FeSO_4 . 7H_2O$ 0.525 g.	0.210	0.523 g.
Micsofer tablet	Napha National Pharmaceuticals	Ferrous gluconate 0.195 g.	0.105	0.194 g.
Ferrofolindione tablet	'Indopharma' Pharmaceuticals	Ferrous fumarate 0.2 g.	0.130	0.198 g.
Iberol-liquid	Abbott Laboratories Private Ltd.	$FeSO_4 . 7H_2O$ 0.131 g.	0.105	0.130 g.
Tonoferon drops	East India Pharmaceutical Works	Colloidal iron hydroxide 50 mg.	0.100	47.9 mg.

Ferric Nitrate : 0.005 *M* solution was prepared by dissolving requisite amount in distilled water.

Sodium Perchlorate : 1 *M* solution was prepared in distilled water.

Procedure :

2 ml solution of ferric nitrate was taken in a beaker. 20 ml solution of β-resorcylaldehyde was added to it giving violet colour. 5 ml solution of sodium perchlorate was added to give an ionic strength of 0.1 *M* and *p*H of solution was adjusted by adding nitric acid. The final volume was made 50 ml. The solution was allowed to stand for 30 minutes. The absorbance was measured at different wavelengths using distilled water as blank.

Absorption Characteristics at Different pH :

The absorption characteristics of the complex in the *p*H range 1.0-3.0 showed that β-resorcylaldehyde gave a maximum colour at *p*H 2.5, stable for 24 hrs. The *p*H was adjusted with dil. nitric acid. The maximum absorption of light was shown by β-resorcylaldehyde complex in the region 420-460 nm. The depth of colour was not affected by the sequence of adding the reagent.

Composition of the Complex :

The composition of complex was studied by mole ratio method, method of continuous variation and slope ratio method. The formation of 1 : 1 complex was indicated and the stability constant was evaluated to be 3.786×10^{3}.

Optimum Concentration Range and Obeyance of Beer's Law :

The optimum concentration was 0.105 mg to 0.25 mg per 25 ml with β-resorcylaldehyde. Beer's Law was obeyed in the concentration range 1-56 ppm.

Effect of Diverse Ions :

It was found that 40 ppm of Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Cd^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Cu^{2+}, or Ni^{2+} and 20 ppm of Mn^{2+}, Al^{3+}, Th^{4+}, K^{+}, NH_4^{+}, SO_4^{2-}, Cl^{-} and NO_3^{-} could be tolerated provided a limit of 3% change in absorbance was allowed. It was found that NO_2^{-}, HCO_3^{-}, I^{-}, PO_4^{3-} and F^{-} interfered at all levels.

The suggested procedure was successfully applied to the analysis of pharmaceuticals containing iron in the form of colloidal iron hydroxide, ferrous gluconate, ferrous fumarate and ferrous sulphate. Liquid drugs containing ferrous sulphate or ferric hydroxide were diluted with distilled water and 2 ml con. HNO_3 was added. The mixture was heated for 10-15 minutes, cooled and diluted to one litre.

Tablets or capsules containing ferrous sulphate, ferrous fumarate or ferrous gluconate were treated with 10 ml con. HNO_3 and 2 ml $HClO_4$. The mixture was evaporated to dryness. The residue was diluted to one litre. 1 ml aliquot of diluted solution was used for measuring absorbance at *p*H 2.5. The results are given in Table 1.

Conclusion :

In phenolic aldehydes the substitution of H atom in position 4 by an OH group was most favourable as (the extinction coefficients of salicylaldehyde and β-resorcylaldehyde were 1125 and 2187) shown by the study of extinction coefficient of salicylaldehyde and β-resorcylaldehyde.

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Chemical Constituents of *Clerodendron infortunatum* Linn. and *Ficus racemosa* Linn.

KRISHNA C. JOSHI, LALIT PRAKASH
and
RAMA KANT SHAH
Department of Chemistry, University of Rajasthan,
Jaipur-302004

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CLERODENDRON infortunatum Linn. (Verbenaceae) is a shrub and found throughout India. All parts of the plant have a bitter pungent taste. The leaves are used externally for tumors and certain skin diseases[1]. A perusal of literature revealed that some work has been reported on the roots[2-5] and leaves[6] of this plant. The present investigation deals with the isolation and identification of the constituents from flowers.

Ficus racemosa Linn. (Moraceae), a moderate sized tree, is an important medicinal plant[7]. The roots[8] and leaves[9] of this plant have been earlier investigated. A chemical investigation of the bark and heartwood of the plant has, therefore, been undertaken.

C. infortunatum : The air dried flowers (2 Kg.) were extracted with petroleum ether (60-80°). The extract was concentrated to 100 ml. On cooling and filtration a solid material was obtained (Fraction-A). The filtrate was concentrated to dryness (Fraction-B).

Fraction-A, on column chromatography over deactivated alumina and elution with petroleum ether, gave a solid which on crystallization (pet. ether), furnished colourless needles, $C_{24}H_{34}O_7$, m.p. 164°. It gave positive Liebermann-Burchard and Noller's test. ν_{max}^{Nujol} 1730, 1250, 1018, 735 cm^{-1}, etc.; $\delta(CCl_4)$ 0.92 (s), 1.92-2.10(d), 2.9-3.0(t), 4.8(s), 5.95-6.06(d) and 6.5(t) ; M^+ 434. It was identified as the diterpene clerodin.

Fraction-B, on column chromatography over deactivated alumina, gave two compounds. Elution with petroleum ether yielded a product, which on crystallization from ethyl acetate gave a white solid, $C_{31}H_{64}$, m.p. 67°. ν_{max}^{Nujol} 730, 720 cm^{-1} [doublet, $-(CH_2)_n-$ bending, $n>4$]. It was identified as hentriacontane by m.m.p., Co-TLC with an authentic sample.

Further elution with petroleum ether-benzene (4 : 1), gave a greenish-white solid which on crystallization (pet. ether) gave colourless needles, $C_{29}H_{46}O$, m.p. 148°. ν_{max}^{Nujol} 3400-3200 1630, 960, 885, 795 cm^{-1}, etc. It was identified as (24s)-ethylcholesta-5,22,25-triene-3β-ol by m.m.p. and Co-TLC with an authentic sample.

F. racemosa : The dried and powdered bark (2 Kg.) was extracted with petroleum ether (60-80°). The extract was concentrated and chromatographed over deactivated alumina. Elution with petroleum ether and crystallization from methanol gave compound A, $C_{32}H_{52}O_2$, m.p. 184°. It gave positive Liebermann-Burchard, Noller's and TNM tests. ν_{max}^{KBr} 1750, 1450, 1380, 1365, 1240, 975 cm^{-1}, etc. M^+468. Compound A was identified as gluanol acetate.

Elution with petroleum ether-benzene (1 : 1) and benzene and crystallization from methanol gave shining white flakes of compound B, m.p. 136-37°. It was identified as β-sitosterol by m.m.p. and Co-TLC with an authentic sample, and preparation of its acetate, m.p. 127° and benzoate, m.p. 143°.

In addition a small amount of a long chain ketonic compound, m.p. 72° was also isolated.

Heartwood shavings (5 Kg.) were extracted with petroleum ether (60-80°). The pet. ether extract was chromatographed over deactivated alumina. Elution with petroleum ether yielded a product which was identified as gluanol acetate and elution with benzene gave β-sitosterol.

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Potential Antituberculosis Compounds : Part I. Substituted Thioureas Containing Quinoline Nucleus*

K. V. KALE and S. N. KULKARNI
National Chemical Laboratory, Poona-8

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ANTIBACTERIAL property of thiourea was observed by E. Nicholas[1] in 1928 and Mayer in 1941[2]. Sulphanilamido thiourea and phenyl sulphanilamido thiourea were found to be very active against

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tuberculosis, *in vitro*[2]. A large number of diaryl substituted thioureas have been prepared by various workers[3,4,5,6] so far and a good number of them were found to be active. It is interesting to find out whether, the replacement of one of the aryl rings by a para substituted quinoline ring does increase the activity or not. Quinoline ring was of interest as 8-alkoxy quinolines and aminoquinolines are generally bacteriostatic[7,8].

$$R-NH-\overset{\overset{S}{\|}}{C}-NH-C_6H_4-(p)R^1$$

No.	R	R^1	M.P.*	** Activity Micrograms per ml
1		$-OCH_3$	192°	40.0
2		$-OC_2H_5$	154°	0.5
3		$-OC_4H_{9(n)}$	164°	0.5
4		$-OC_4H_{9(iso)}$	165°	2.0
5	8-ethoxy-5-quinolyl	$-OC_5H_{11(n)}$	170°	0.5
6		$-OC_5H_{11(iso)}$	176°	5.0
7		$-CH_3$	198°	10.0
8		$-Cl$	186°	40.0
9		$-N(CH_3)_2$	193-194°	100.0
10		$-H$	184°	100.0
11		$-OCH_3$	170°	5.0
12		$-OC_2H_5$	150°	0.5
13		$-OC_4H_{9(n)}$	151°	0.2
14		$-OC_4H_{9(iso)}$	160°	1.0
15	8-*n*-butoxy-5-quinolyl	$-OC_5H_{11(n)}$	184°	0.5
16		$-OC_5H_{11(iso)}$	152°	5.0
17		$-CH_3$	172°	20.0
18		$-Cl$	178°	40.0
19		$-N(CH_3)_2$	183°	100.0
20		$-H$	175°	100.0
21		$-OCH_3$	151°	5.0
22		$-OC_2H_5$	158°	0.5
23		$-OC_4H_{9(n)}$	165°	2.0
24		$-OC_4H_{9(iso)}$	178°	2.0
25	8-chloro-5-quinolyl	$-OC_5H_{11(n)}$	177°	0.5
26		$-OC_5H_{11(iso)}$	198°	10.0
27		$-CH_3$	187°	40.0
28		$-Cl$	179°	20.0
29		$-N(CH_3)_2$	170°	100.0
30		$-H$	168°	100.0
31		$-OCH_3$	177°	10.0
32		$-OC_2H_5$	150°	0.5
33		$-OC_4H_{9(n)}$	145-146°	2.0
34		$-OC_4H_{9(iso)}$	141°	5.0
35	5-chloro-8-quinolyl	$-OC_5H_{11(n)}$	127°	0.5
36		$-OC_5H_{11(iso)}$	138°	5.0
37		$-CH_3$	179-180°	5.0
38		$-Cl$	174° d	100.0
39		$-N(CH_3)_2$	163-164° d	100.0
40		$-H$	174°	40.0
41		$-OCH_3$	146°	5.0
42		$-OC_2H_5$	161°	0.5
43		$-OC_4H_{9(n)}$	146°	0.2
44		$-OC_4H_{9(iso)}$	139-140°	5.0
45	6-quinolyl	$-OC_5H_{11(n)}$	153°	0.5
46		$-OC_5H_{11(iso)}$	133°	2.0
47		$-CH_3$	131°	2.0
48		$-Cl$	158-159°	5.0
49		$-N(CH_3)_2$	108°	100.0
50		$-H$	163°	40.0

* All the m.ps. are uncorrected and depend on the speed of heating.

** Micrograms/ml for (i) INH = 0.04
(ii) Streptomycin = 1.0.

The present communication describes diaryl substituted thioureas in which, one of the aryl ring is substituted by a substituted quinoline ring. These have been prepared by refluxing the substituted aminoquinolines with different aryl isothiocyanates in ethanol. The yields range from 60-80%. All the prepared compounds are new and gave correct elemental analysis. All the compounds were tested *in vitro*. The results of the testing are expressed is minimum inhibitory concentration in micrograms/ml Compounds having $-OC_2H_5$, $-OC_4H_{9(n)}$ and $-OC_5H_{11(n)}$ in para position of the phenyl ring were found to be more active.

Acknowledgements

We wish to thank the Council of Scientific and Industrial Research for a Junior Research Fellowship to one of us (KVK).

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Solid State Studies on Polymerization and Depolymerization of Tungstate Ion with Mn(IV) as the Hetero-atom

H. C. MISHRA and SALIL KUMAR ROY

University Department of Chemistry, Ranchi University, Ranchi-8.

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A new polymeric compound, $Na_4[MnW_{12}O_{40}]$ $32H_2O$, has been prepared and characterised on the basis of analytical and molecular weight determinations. The oxidation state of the central manganese(IV) ion has been established by magnetic and e. s. r. data. The thermal depolymerization of the compound has been studied extensively in solid state.

25 grams of sodium tungstate in water (200 ml) was heated to 90° and a mixed solution of manganese(II) sulphate (5 g.) in water (50 ml) and

sodium peroxidisulphate (7 g.) in water (100 ml) was added dropwise, with vigorous stirring. To the resulting solution, acetic acid was added till *p*H comes just in the range of 3.7 to 4.0. The solution was boiled for an hour, left overnight and crystallised under vacuum when bright orange needle-shaped crystals of sodium 12-tungstomanganate(IV) separated which were recrystallised from hot water (Found : Na, 2.41 ; W, 60.99 ; Mn, 1.42 ; H, 1.85% Calcd. for $Na_4[MnW_{12}O_{40}]$ $32H_2O$: Na, 2.50 ; W, 61.14 ; Mn, 1.53 ; H, 1.85%). Hydrogen has been estimated by element estimation method and tungsten has been determined[1] by precipitating it as tungstic acid with Hcl and cichonine hydrochloride, igniting it at 780° and finally weighing as WO_3. Sodium was estimated by flame photometer and manganese was volumetrically determined by bismuthate method[2]. From the analytical data, the molecular formula of the compound, as per Keggin's view[3], comes out to be Na_4 $[MnW_{12}O_{40}]$ $32H_2O$, which falls under the category of heteropoly compounds.

Molecular weight determinations : The cryoscopic method as has been applied successfully by Alexander[4] and by Thilo and Kruger[5] for molecular weight determinations of polymerised silicic acids, condensed phosphates, etc., in water and molten sodium sulphate decahydrate ; has also been applied here for determination of approximate molecular weight of the compound. This determination showed the molecular weight of the polymeric compound to be 3470 as compared with the calculated value 3569.22. To know the accurate degree of polymerisation this result has been corroborated by X-ray crystal diffraction technique[6,7] for molecular weight determination of heteropoly salts. The crystal diffraction data of the compound are a = 12.56, b = 30.22, c = 11.40 and $\alpha = \beta = \gamma = 90$, volume per unit cell 'V' = 4327.02$Å^3$. The space group is established as $D_{2h}^{2} - P_{nnn}$ from the following systematic presence of reflections : hkl = no condition ; 0kl = k+l = 2n ; h0l = l+h = 2n ; hk0 = h+k = 2n ; h00 = (h = 2n) ; 0k0 = (k = 2n) ; 00l = l = 2n and hkl = h+k+l = 2n. The last condition gives the no. of molecules in unit cell (z) to be 2. Pycnometric measurement gives the observed density, $\rho_{obs.} = 2.71$ gml^{-1}. From the relation[8], $\rho_{obs.} = 1.66$ M.Z/V, the molecnlar weight 'M' of the compound comes to 3646 against the calculated value 3569.22.

Determination of oxidation state of manganese ion : e.s.r. spectrum of heteropoly molybdomanganate and heteropoly tungstomanganate in frozen aqueous solution at 77° K have been measured. Both the compounds showed broad asymetric signals with g = 3.8. This is an expected value[8] for a trigonally distorted d^3 ion. The effective magnetic moment of 12-sodium tungstomanganate(IV) was found by susceptibility measurements, the values being 3.88 B.M. at 302° and 3.89 B.M. at 77°K. Both the values are close to the spin-only for an S = 3/2 ion, as expected[8] for $3d^3$ system (three unpaired electrons), which definitely concludes that central heteroatom, Mn, is in +4 oxidation state.

Thermal depolymerization : The thermal depolymerization of the compound has been studied in the light of the investigations made by West and Audrieth[9] on a few heteropoly tungstic acid. Use was made of the apparatus described by Ray and Sinha[10] with continuous pumping the depolymerised product, followed by successive weighing using a thermogravimetric balance and estimating at some stages. The dissociation[6] of the compound was observed at 75° under reduced pressure when seven molecules of water was lost. At 140°, further twelve molecules of water were eliminated. The rest of water molecules remained intact in the crystal latice till 290°, above which they were completely removed. When the temperature was raised still higher, then nearly at 480° ± 5°, the compound was broken as a whole into the basic units of lower oxides of tungsten and manganese which have been confirmed by analysis. So the thermal stability of sodium-12-tungstomanganate(IV) is 480° ± 50.

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Formation Constants of Tl(I)-5-Nitro Salicylates and Effect of Nitro Substituent on the Formation Constants

P. V. KHADIKAR

School of Studies in Chemistry, Vikram University, Ujjain, (M.P.).

and

P. S. DESHMUKH*

Govt. College, Khargone, (M.P.).

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IN continuation to the previous work on Tl(I)-complexes of 3-Nitrosalicylic acid (3NSA)[2], and 3 : 5-Dinitrosalicylic acid (3 : 5 DNSA)[3], the

* Address for correspondence : Gymkhana Road, Khargone, (M. P.). 451 001

proton-ligand formation constants and formation constants of 5-Nitrosalicylic acid (5NSA) with Tl(I) ion have been determined at 30°, using different computational methods viz. Half integral (HI), linear plot (LP), and point-wise calculation (PC), methods. Refined values of formation constants are obtained by the method of least-squares(LS).

To study the effect of the nitro substituent on the protonation and the stability of Tl(I)-complexes of salicylic acid with reference to its position, proton-ligand formation constants and formation constants of salicylic acid (SA) have also been determined under the same experimental conditions. Results with 3-NSA[2] and 3 : 5-DNSA[3] under the same experimental conditions, are already reported.

Experimental

*p*H-metric titrations of following sets were carried out at 30° :—

(i) Free $HClO_4$ (ii) free $HClO_4$+ligand and (iii) free $HClO_4$+ ligand +Tl(I), in 50% (V/V) aqueous thianol medium against standard NaOH solution while maintaining the ionic strength at 0.1 *M* $NaClO_4$.

The experimental set up and the method of calculation is the same as described earlier.

Results and Discussion

The Irving-Rossotti expression[1] was used for the calculation of $\bar{n}_A$, $\bar{n}$ and p(L). The values of log K^H_n and log K_n were directly recorded from the respective formation curves by half-integral method. Proton-ligand formation constants and formation constants of complexes are also calculated by linear plot and point-wise calculation method using equation :—

$$\log K_n = p(L)_{n-\frac{1}{2}} \quad \text{(Ref. 8)}$$

and

$$\log K^H_n = pH_{n-\frac{1}{2}}$$

Refined values of formation constants are obtained by the method of least squares. Values are recorded in Table 1.

The ratio of log K_1/K_2 is positive in both the cases. A difference between log K_1 and log K_2 is because of possible steric hindrance on the linking of the second ligand molecule.

In both the cases $\bar{n}$ value never exceeds 1.75, indicating thereby formation of only 1 : 1 and 1 : 2 complexes. Estimation of elements in the complexes isolated, also indicates 1 : 2 ratio of metal to ligand in both the cases.

Effect of Nitro group :

The order of log K^H_1 of the ligands used in the present investigation is : (Table 2)

SA>5-NSA>3-NSA>3 : 5-DNSA

and that of log K^H_2 is :

SA>5-NSA≃3-NSA>3 : 5-DNSA

where log K^H_1 represents protonation with phenoxide group and log K^H_2, protonation with carboxylate group. The results are in agreement with the inductive and resonance effect of nitro group in each case.

The order of overall basicity (log K^H_β) is :

SA>5-NSA>3-NSA>3 : 5-DNSA

TABLE 1

PROTON-LIGAND FORMATION CONSTANTS AND FORMATION CONSTANTS OF Tl(I)-COMPLEXES

Method	Salicylic acid and its complexes						5-Nitrosalicylic acid and its complexes					
	log K^H_1	log K^H_2	log K^H_β	log K_1	log K_2	log K_β	log K^H_1	log K^H_2	log K^H_β	log K_1	log K_2	log K_β
HI	**(11.40)	3.21	14.61	8.95	5.00	13.95	10.76	2.28	13.04	8.28	5.44	13.72
LP	12.00	3.20	15.20	8.95	5.02	13.97	10.76	2.28	13.04	8.28	5.43	13.71
PC	12.29	3.20	15.49	8.75	5.07	13.82	10.76	2.20	12.96	8.29	5.45	13.74
LS				8.94	5.12	14.06				8.29	5.43	13.72

** Value is calculated from log K^H_β

TABLE 2

PROTON-LIGAND FORMATION CONSTANTS OF LIGANDS — FORMATION CONSTANTS OF Tl(I)-COMPLEXES

	log K^H_1	log K^H_2	log K^H_β	log K_1	log K_2	log K_β
SA	11.73	3.20	14.93	8.90	5.05	13.95
3-NSA	10.34	2.30	12.64	7.87	5.05	12.92
5-NSA	10.75	2.26	13.01	8.28	5.44	13.72
3 : 5-DNSA	8.17	2.04	10.21	6.21	4.38	10.59

The order of formation constants of Tl(I)-complexes (Table 2) is :

Tl(I)-SA>Tl(I)-5-NSA>Tl(I)-3NSA>Tl(I)-3 : 5-DNSA

This is in agreement with the basicities of the ligands. Decrease in the stabilities of the complexes, is in agreement with the expectation of steric effect[4,5] of nitro substituent for Tl(I) ion in each case because of its large size and position in different ligands.

Results indicate the failure of Hammett's equation[6] and Taft's equation[7] in the ligands as well as in complexes.

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Letter to the Editor

Dear Sir,

Recently we have come across a paper entitled, "Mossbauer Studies on some Fe(III) complexes" by C. L. Sharma, Ashok Kumar Singh and Lakshmi Devi[1] published in this journal. In this connection we would like to point out that we have published in 1970 a paper entitled, "Mossbauer Studies on some iron(III) complexes".[2] The complexes investigated by us included [Fe(Saccharin)$_2$Cl], K[Fe(3-nitrophthalimide)$_4$2CH$_3$OH] and [Fe(benzofuryl carboximide-N-*p*-toluenesulphonyl)$_3$]. Though the complexes investigated by Sharma *et al*[1] are naturally different, there is a considerable overlap in the language employed in the recent paper as compared to ours. In fact at a number of places in the text their paper appears to be a verbatim copy of our paper except that the names of the complexes are different, although our paper has not been cited by them.

We are thankful to the Hon.Editor for giving us an option to present our views.

Chemistry Division,
Bhabha Atomic Research Centre,
Trombay, Bombay 400 085.

V. RAMSHESH

K. S. VENKATESWARLU

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Book Review

MTP International Review of Science : Inorganic Chemistry, Series One, Vols. 1-10 (3631 pages), Index volume (200 pages), H. J. Emeleus (Consulting Editor), Butterworths, London, 1972. Price, £ 10.00 per volume.

THE astonishingly fast developments in the field of Inorganic Chemistry in recent years due to wide scale application of physical methods and theories has also ushered in much greater systematization and correlation in the subject. This review series is a documentation of the significant progress in the different areas of inorganic chemistry that took place over a period of five years or so, beginning in 1966.

Volume 1 deals with advances in the chemistry of hydrogen and of the alkali and alkaline earth metals, Be, Mg, Zn, Cd, Hg, B, C (excluding typically organic compounds), Si, Ge, Sn and Pb, including a chapter on the carboranes and metallocarboranes. Volume 2 deals with certain aspects of the chemistry of several elements of Groups V and VI of the Periodic Table, viz., N, P, As, O, S, Se and Po. Volume 3 deals with the advances in the chemistry of the noble gases and certain aspects of the chemistry of the members of the halogen family including astatine. Volume 4 has several articles dealing with the most significant developments of the period in the field of organometallic compounds of the metals of the main group elements such as those of Groups IA, IIB, IIIA (including boron), IVA(including silicon) and VA. A review on similar compounds of Group IIA metals is, however, missing and the editors have promised to include this in the next issue of the review series. Volumes 5 & 6 are on transition metal chemistry. Volume 5 is specially devoted to a survey of the developments in the field of simple compounds of these elements and volume 6 deals with a survey on the transition metal carbonyls, complexes of these metals with ligands having phosphorus, arsenic, antimony and bismuth as donors, organometallic compounds of transition metals, etc. Volume 7 covers several aspects of lanthanide and actinide chemistry including separations of individual members of each family and studies on the chemistry of these elements and their principal compounds including organometallic compounds and complexes and spectral features of actinide compounds. Volume 8 is devoted to developments in radiochemistry and chemistry of some of the heavier members of the trans-uranium series of elements and on the possible existence of super-heavy elements. Volume 9 reviews some of the significant advances in the field of mechanistics of different types of inorganic reactions, including fast reactions of non-transition metals, photochemistry of inorganic compounds and thermodynamics of complex formation in solution. Volume 10 is a review on those areas of solid state chemistry as are of interest to inorganic chemists including mechanisms of reactions in the solid state, electrical conductivity in ionic solids, non-stoichiometric compounds, etc. There is also an Index Volume for the series which helps the reader to locate easily the subject areas of his interest. Every chapter of each of the ten volumes is written by acknowledged authorities in the fields and each such chapter ends with comprehensive literature citations which increases further the utility of this review series.

Professor Emeleus, the consulting editor of this series, the editors of the different volumes and the contributors of the different articles appearing in each volume have really done a splendid job in their commendable efforts in bringing an immense wealth of information within the easy reach of the research workers, and all those interested in recent developments in different areas of the subject. By bringing out this series the publishers have also earned the gratitude of all the users of this useful reference series. The reviewer earnestly hopes that such efforts of the publisher continue unabated in future also for the benefit of the students, teachers and research workers in inorganic chemistry. He definitely considers this series worthy of possession.

D. Banerjea

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Some New Reagents for Keto-Steroids—Part II

N. THAKKAR and C. N. HAKSAR

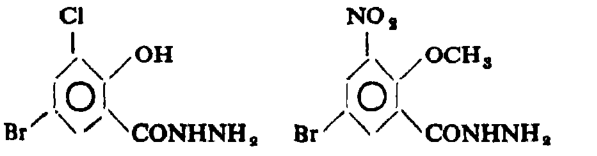
School of Post-graduate Studies and Research in Chemistry, Jiwaji University, Gwalior (M. P.)

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2-Methoxy-3-bromo-5-chlorobenzohydrazide and 2-methoxy-3-nitro-5-chlorobenzohydrazide form good crystalline hydrazones with three ketosteroids, namely estrone, dehydro-epiandrosterone and 5-β-androsterone[1]. Similarly 2-hydroxy-3-chloro-5-bromobenzohydrazide and 2-methoxy-3-nitro-5-bromobenzohydrazide have now been synthesised and their reactivity towards some ketosteroids has been studied.

THE conventional method for characterisation and estimation of the ketosteroid hormones is to employ Girard reagents P and T[2]. This method has its limitations and has been modified by Walter[3]. Certain other hydrazides like nicotinic hydrazide and benzilic hydrazide which form insoluble hydrazones with carbonyl compounds have also been used for the preparation of hydrazones from ketosteroids[4]. Several new benzohydrazides as prospective reagents for the ketosteroids have been recommended by Haksar and Wankhade[5] and Haksar and Sethi[6].

Two new substituted benzohydrazides namely, 2-hydroxy-3-chloro-5-bromobenzohydrazide (I) and 2-methoxy-3-nitro-5-bromobenzohydrazide (II) have now been synthesized by us by the action of 60% hydrazine hydrate, on the corresponding esters.



I II

The reactivity of these hydrazides towards three ketosteroids namely estrone, dehydroepi-androsterone and 5-β-androsterone has been found to be satisfactory and crystalline hydrazones have been isolated in good yield in all the three cases.

Experimental

Methyl 2-hydroxy-3-chloro-5-bromobenzoate :

Methyl 2-hydroxy-5-bromobenzoate has been prepared by the bromination of methyl—salicylate using bromine and acetic acid mixture in acid medium[7]. It was then chlorinated to obtain methyl 2-hydroxy-3-chloro-5-bromobenzoate by using conc. hydrochloric acid and hydrogen peroxide (30%, 100 vols) by slightly modifying the method of A. Leulier and L Pinet[8]. Methyl 2-hydroxy-3-chloro-5-bromobenzoate was crystallised from hot water, as long colourless needles, m.p. 154°.

(Found C, 35.72%, H, 2.10%; $C_8H_6O_3BrCl$ requires C, 36.17%; H, 2 26%)

2-Hydroxy-3-chloro-5-bromobenzohydrazide-(I) :

A solution of methyl 2-hydroxy-3-chloro-5-bromobenzoate (4 gm. dissolved in 90 ml. of methanol) was mixed with 60% hydrazine hydrate (10 ml.) in warm condition and then refluxed for 20 mins. on a steam bath. It was then cooled, diluted with double its amount of water and then 2-3 drops of acetic acid were added to this solution when a white solid separated. It was filtered, washed with aqueous methanol and dried. Yield 3.5 gm. (crude). Crystallisation from aqueous methanol gave colourless micro needles, m.p. 184°.

The I.R. spectrum of (I) showed the characteristic bands at 1655 (Carbonyl), 1600 (Aromatic), 765 (Chlorine), 3500 (hydroxyl) and 2900-3300 cm^{-1}. (–NH).

(Found C, 31.15%; H, 2.76%, N, 10.19%; $C_7H_6O_2N_2BrCl$ requires C, 31.65%; H, 2.26%; N, 10.55%).

Methyl 2-methoxy-3-nitro-5-bromobenzoate :

The 5-bromo derivative of salicylic acid[7] was methylated by slightly modifying the method of F. Sachs and V. Harold[9]. Methyl 2-methoxy-5-bromobenzoate so formed was then nitrated to obtain methyl 2-methoxy-3-nitro-5-bromo-benzoate using the method of Hirsch[10]. Nitration was carried out at 0° by using a nitrating mixture of conc. sulphuric acid and conc. nitric acid. Yield 75%. It was crystallised from methanol as yellow needles, m.p. 124°.

(Found C, 36.57%; H, 2.05%; N, 4.44%; $C_9H_8O_5NBr$ requires, C, 37.25%; H, 2.75%; N, 4.82%)

2-Methoxy-3-nitro-5-bromobenzohydrazide (II) :

A solution of methyl 2-methoxy-3-nitro-5-bromobenzoate (2 gm.) in methanol (2 ml.) was treated with 60% hydrazine hydrate (5 ml.) and refluxed on a steam bath for 30 mins. The rest of the procedure was repeated as mentioned in the case of hydrazide (I). Crystallisation

from aqueous dioxan (9 : 1) gave yellow micro needles, m.p. 276° (decomp.).

The I.R. spectrum of the (II) showed the characteristic bands at 1650 (Carbonyl), 1580 (Aromatic), 3000-3360 (NH) and 1530 cm^{-1} (Nitro).

(Found C, 32.91% ; H, 2.15% ; N, 14.08% ; $C_8H_8O_4N_3Br$ requires C, 33.11% ; H, 2.75% ; N, 14.48%).

Hydrazones of estrone—

(i) *With 2-hydroxy-3-chloro-5-bromobenzohydrazide (I)* : 2-Hydroxy-3-chloro-5-bromo-benzohydrazide (0.2 gm.) was dissolved in methanol (12 ml.). Estrone (0.2 gm. dissolved in 25 ml. of methanol) and acetic acid (0.2 ml.) were added to it and the reaction mixture was refluxed for 30 mins and then concentrated by removing methanol under reduced pressure. It was cooled in ice and diluted with cold water. A bulky white precipitate appeared after some time which was filtered, washed with a small quantity of aqueous methanol and dried. Yield 62%. Itwas crystallised from methanol when colourless micro needles were obtained, m.p. 196°.

(Found C, 57.63% ; H, 4.91% ; N, 4.84% ; $C_{25}H_{26}O_3N_2ClBr$ requires C, 57.96% ; H, 5.02% ; N, 5.41%)

(ii) *With 2-methoxy-3-nitro-5-bromobenzohydrazide-(II)* : 2-Methoxy-3-nitro-5-bromobenzohydrazide (0.2 g.) was dissolved in absolute alcohol (30 ml.). Estrone (0.2 gm. dissolved in 30 ml. of absolute alcohol) was added to it. To the reaction mixture glacial acetic acid (0.2 ml.) was added and the reaction was carried out further as described above. Yield 75%. It was crystallised from absolute alcohol, when light yellow colour needles were obtained, m.P. 234° (decomp.).

(Found C, 57.18% ; H, 4.82% ; N, 7.12% ; $C_{26}H_{28}O_5N_3Br$ requires C, 57.57% ; H,5.16% ; N, 7.75%.)

Hydrazones of dehydro-epiandrosterone—

(i) *With 2-hydroxy-3-chloro-5-bromobenzohydrazide-(I)*. The preparation was carried out as described in the case of estrone.

Yield 50%. Colourless needles, m.p. 166°.

(Found C, 57.82% ; H, 6.25% ; N, 4.90% ; $C_{26}H_{32}O_3N_2ClBr$ requires C, 58 27% ; H, 5.97% ; N, 5.22%)

(ii) *With 2-methoxy-3 nitro-5-bromobenzohydrazide-(II)*. The procedure was same as in the case of estrone. Yield 45%. Yellow colour micro needles, m.p. 150°.

Found C, 57.21% ; H, 5.91%, N, 6.82% ; $C_{27}H_{34}O_5N_3Br$ requires C, 57.86% ; H, 6.07% ; N, 7.50%)

Hydrazones of 5-β-androsterone—

(i) *With 2-hydroxy-3-chloro-5-bromobenzohydrazide-(I)* The preparation was carried out as described in the case of estrone.

Yield was found to be 60%, colourless needles, m.p. 110°.

(Found C, 57.82% ; H, 6.25% ; N, 5.29% ; $C_{26}H_{34}O_3N_2BrCl$ requires C, 58.03% ; H, 6.32% ; N, 5.21%).

(ii) *With 2-methoxy-3-nitro-5-bromobenzohydrazide-(II)*. The procedure was same as in the case of estrone.

Yield 40%. Yellow colour micro needles, m.p. 210° (decomp.).

(Found C, 57.95% ; H, 6.02% ; N, 8.21% ; $C_{27}H_{36}O_5N_3Br$ requires C, 57.66% ; H, 6.40% ; N, 7.47%).

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Adsorption of Stearic Acid on Pure and Mixed Oxides

R. L. MADAN* and N. K. SANDLE

Chemistry Dept., Indian Institute of Technology, New Delhi (India)

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The adsorption of stearic acid from solutions in cyclohexane on tin oxide (in the form of gel and precipitate), antimony oxide and tin-antimony mixed oxides having various ratios of tin to antimony, has been investigated. It is observed that the mode of adsorption depends upon the surface acidity of the oxide. In the case of tin oxide gel, tin oxide ppt. and the mixed oxides with Sb : Sn as 1 : 5 and 1 : 10, stearic acid is adsorbed with its hydrocarbon chain parallel to the surface. With antimony oxide and mixed oxides with higher percentage of antimony, the perpendicular orientation is adopted.

THE adsorption of long chain fatty acids from solutions in organic solvents has frequently been used for evaluating surface characteristics of solids[1]. It has been observed that stearic acid adsorbs itself from its solutions in cyclohexane parallel to the surface of homogeneous carbons. A similar orientation is preferred by stearic acid from its solutions in inert solvents on silica[2]. But it has been reported that a perpendicular orientation is adopted by the long-chain fatty acids on alumina and titania[1-2].

It is revealed on perusal of literature that adsorption studies on tin oxide and antimony oxide have not been carried out to an appreciable extent. Some recent studies have proved that tin oxide, antimony oxide and their mixtures act as efficient and highly selective catalysts in a number of industrial processes particularly the dehydrogenation of olefins[3]. Surface area, surface acidity, particle size, conductivity measurements[4] and solid state studies[5] have been used to characterise the surface of the active solids. In order to obtain more information about the nature of the surface of these oxides, it was thought of interest to study the orientation of stearic acid adsorbed onto tin oxide (gel and precipitate), antimony oxide and their co-precipitated mixtures having varying percentages of Sn and Sb. Similar adsorption studies form n-hexane-benzene[6], alcohol-hydrocarbon[7] and fatty acid hydrocarbon[8] solutions has been reported earlier. In the present paper, the observed adsorption values have been compared with the values calculated on the basis of various orientations. For one of the samples (SnO_2 gel), the composite isotherm has been analysed by the Schay and Nagy[9] method to yield the individual adsorption isotherms.

Experimental

Preparation of materials: The oxide gel was prepared by mixing equal volumes of 1.2 *N* ammonia solution and 1.0 *N* solution of stannic chloride[4]. Tin oxide and antimony oxides were prepared by treating pure tin and antimony metals separately with conc. nitric acid and washing the products with distilled water till free from NO_3^- ions. Mixed oxides were prepared in a similar way by treating calculated quantities of tin and antimony metals with conc. nitric acid. All these samples except tin oxide gel were dried in an air oven at 120°. Tin oxide gel was air dried at 30°. All the solids were passed through a 100 mesh sieve to maintain uniformity in their particle size. Cyclohexane was purified by distillation and the fraction distilling at 81° was collected. Cyclohexane was chosen as a solvent to minimise the interaction between the solvent and the adsorbent. TGA analysis of the samples was done on Stanton balance. The stoichiometry of the mixed oxides was confirmed by usual analytical methods[10]. The acidity of the samples was determined by adsorption of barium hydroxide in aqueous solution (Table 3).

Adsorption studies

One g. of the sample was mixed with 10 ml. of the stearic acid solution, of varying concentrations in cyclohexane in each bottle which was sealed and kept in an air-oven maintained at 30±1°. The bottles were shaken occasionally. Reference solutions were also treated in a similar manner. After 24 hours, bottles were unsealed and stearic acid solutions were analysed titrimetrically using hot ethyl alcohol. Adsorption results for the samples are plotted in figs 1-2 in the form of composite isotherms.

Results and Discussion

Tin oxide gel, tin oxide, antimony oxide and mixed oxides were subjected to TGA. In the case of tin oxide gel the results showed a gradual loss of weight from 150 to 600°, thereafter the weight remained unchanged upto 1000°. The loss in weight as reported in case of silica and alumina gels indicates the presence of —OH groups on the surface which on heating decompose to lose H_2O leaving behind =O groups. In case of tin oxide, antimony oxide and mixed oxides, no loss was recorded from 150 to 1000°, which indicated the absence

*Present Address : Chemistry Dept., Government College, Faridabad (India) for correspondence.

of OH groups and presence of oxygen as = O. The nature of surface thus revealed by TGA for the various samples is given in Table.

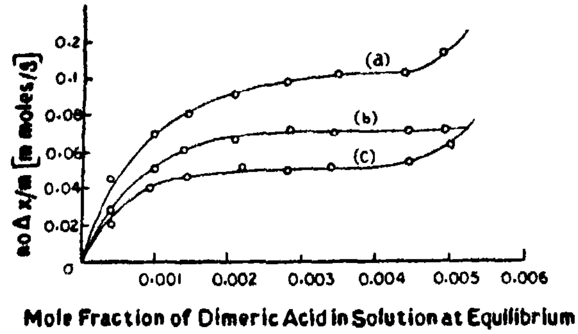


Fig. 1. Adsorption of stearic acid from solutions in cyclohexane.
(a) SnO_2 gel
(b) SnO_2 precipitate
(c) Sb_2O_5

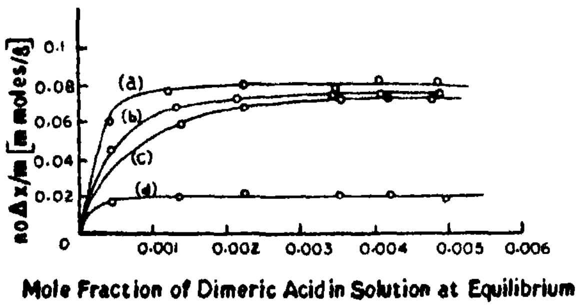


Fig. 2. Adsorption of stearic acid from solutions in cyclohexane.
(a) $10SnO_2.Sb_2O_5$
(b) $10SnO_2.\frac{1}{2}Sb_2O_5$
(c) $2SnO_2.5Sb_2O_5$
(d) $SnO_2.5Sb_2O_5$

TABLE 1—SURFACE AREA AND NATURE OF SURFACE INDICATED BY T.G.A. STUDIES

S. No.	Sample	Surface area from N_2 adsorption (m^2/g)	Nature of the surface (T.G.A. Studies)
1	SnO_2 gel	160	Complete coverage of – OH groups
2	Sb_2O_5	16	= O group only
3	$10 SnO_2.Sb_2O_5$	130	
4	$10 SnO_2.\frac{1}{2}Sb_2O_5$	140	= O group only
5	$SnO_2.5Sb_2O_5$	6.2	
6	$2 SnO_2.5Sb_2O_5$	29.4	
7	SnO_2 ppt	100.00	

Stearic acid is known to be present in the dimeric form[1] in cyclohexane over the whole concentration range used. The mole fractions of the equilibrium solution have been calculated by using the molecular weight of the dimer. As reported by Kipling[11] the surface excess of component I is given by the following equation which is based on the material balance :

$$n_0\Delta x_1/m = n_1^s(1-x_1) - n_2^s x_1 \qquad (1)$$

where Δx_1 is the change in the mole fraction of the component 1 in the bulk phase which takes place when m grams of the adsorbent are brought into contact with n_0 moles of the liquid, x_1 is the mole fraction of the component 1 in the bulk phase at equilibrium and n_1^s and n_2^s are the number of moles of components 1 and 2 respectively adsorbed per g. of the solid. The composite isotherm does not give us the true adsorption of solute, but equation 1 in combination with equation 2, as suggested by Schay and Nagy[9], can be used to calculate n_1^s and n_2^s :

$$\frac{n_1^s}{(n_1)_m} + \frac{n_2^s}{(n_2)_m} = 1 \qquad (2)$$

where $(n_1)_m$ and $(n_2)_m$ are numbers of moles of stearic acid and cyclohexane respectively required to form a monolayer on the adsorbent. The molecular area for cyclohexane has been taken as 45°A². The results for a typical case are shown in figure 3. From the

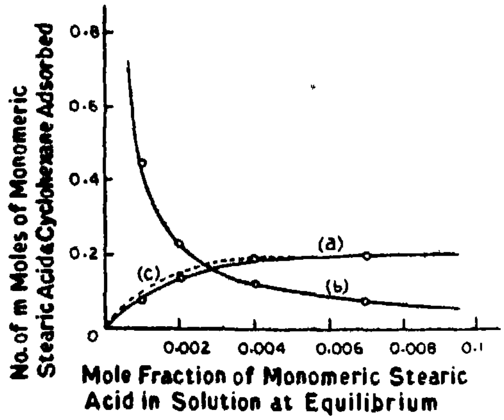


Fig. 3. Individual adsorption isotherms (on tin oxide gel) of (a) stearic acid, (b) cyclohexane, (c) is the composite isotherm for the adsorption of stearic acid.

composite isotherms, it is possible to obtain a limiting value of adsorption from an obvious plateau in the isotherm[1]. These limiting values are compared in Table 2 with calculated monolayer values based on the two orientations for stearic acid with molecular areas (expressed in terms of monomeric molecules) of 114A° for parallel orientation and 20.5A° for perpendicular orientation as reported in the literature[12]. As these molecular areas differ by a factor of approximately five, there is no difficulty in deciding about the orientation actually adopted.

In the case of SnO_2 gel, the ratio of observed monolayer value to calculated monolayer value based on parallel orientation comes out to be 0.9. This proves that stearic acid is adsorbed on the surface of SnO_2 gel in parallel orientation. Similar is the case

TABLE 2

Sample	Calc. monolayer value (millimoles of monomer per g)		Limiting Obs. value (m moles/g)	Rate of Obs. to Calc. value
	Perpendicular orientation	Parallel orientation		
SnO_2 gel	—	.23	.21	0.90
SnO_2 ppt	—	.146	.141	0.96
Sb_2O_5	0.13	—	.065	0.5
$SnO_2.5Sb_2O_5$	0.05	—	.04	0.8
$2SnO_2.5Sb_2O_5$	0.24	—	.12	0.5
$10SnO_2.Sb_2O_5$	—	0.18	.146	0.8
$10SnO_2.\frac{1}{2}Sb_2O_5$	—	0.2	.15	0.75

with SnO_2 ppt where the ratio of observed monolayer to calculated monolayer value based on parallel orientation is 0.96. In the case of antimony oxide the ratio of observed monolayer value to the calculated monolayer value based on perpendicular orientation comes out to be 0.5. It is consistent with the findings in the literature[1] that in perpendicular orientation, a complete monolayer is never formed as the adsorption takes place at specific sites by hydrogen bonding or in some cases by chemisorption as well. The ratio of observed to calculated monolayer values in such cases depends upon the spacing of such sites.

In the case of mixed oxide with Sb:Sn = 10:1 and 5:1 (sample no. 7,8, Table 1), perpendicular orientation is maintained. But the things are reversed when we go to mixed oxides in which Sb to Sn ratio is 1:5 and 1:10 i.e. samples no. 5 and 6 respectively. In these cases because SnO_2 is the major constituent, parallel orientation is adopted. This is revealed by the ratios of observed monolayer values to values calculated on the basis of parallel orientation which come out to be 0.8 and 0.75 respectively.

In cases where parallel orientation is adopted, the observed monolayer value generally falls short of the calculated monolayer value. This may be ascribed to the some amount of solvent in the adsorbed layer where the ratio is 0.9 or 0.96. But the ratios 0.75 or 0.8 can not be explained on the basis of this plea. Assumption of the hydrocarbon chain inclined at some angle instead of being completely flat would perhaps be the satisfactory interpretation.

In the case of SnO_2 gel and Sb_2O_5, the isotherms show a steep rise towards the solubility limit. It is due to phase crystallisation of stearic acid that takes place in this region[11]. It is similar to phase separation[12,13] that takes place in the case of adsorption of liquid solutes from their solutions by silica and alumina catalysts.

The orientation adopted by stearic acid has a direct bearing with the polarity of the surface. The more polar the surface, greater is the tendency for perpendicular orientation. This is evident from Table 3 which gives the surface acidity, for the samples as found out by barium hydroxide adsorption. SnO_2gel, SnO_2 and mixed oxides with Sb to Sn ratio 1:5 and 1:10 have lower surface acidities (columm 3, Table 3). Therefore stearic acid prefers a parallel orientation on these surfaces. On the other hand Sb_2O_5 and mixed oxides, in which Sb to Sn ratio is 10:1 and 5:1, have surface polarity of the higher order; thereby adsorbing stearic acid in perpendicular orientation probably due to higher heat of adsorption.

TABLE 3—EXPERIMENTAL AND NORMALISED BASE ADSORPTION VALUES OF THE ADSORBENTS

Sample	Surface acidity $Ba(OH)_2$ adsorption value (m. equivanlent/g)	Base adsorption value (After normalising for surface area) m. eq'/100 m^2
SnO_2 gel	0.85	0.53
SnO_2 ppt	1.54	1.54
Sb_2O_5	1.10	7.00
$SnO_2.5Sb_2O_5$	1.19	20.00
$2SnO_2.5Sb_2O_5$	1.29	3.90
$10SnO_2.Sb_2O_5$	1.70	1.30
$10SnO_2.\frac{1}{2}Sb_2O_5$	1.66	1.20

For a system with a sufficiently low solubility limit as in this case, the individual isotherm would be indistinguishable from the composite isotherm within the limits of experimental error (c.f. figure 3a as individual isotherm and 3c as composite isotherm).

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The Kinetics of the Decarboxylation of Quinaldinic Acid in Catechol and *o*-Cresol

M. A. HALEEM and M. A. HAKEEM

College of Engineering, University of Riyadh, Riyadh, Saudi Arabia.

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The decomposition of quinaldinic acid has been studied over the range 140 to 180° in the solvents catechol and *o*-cresol. The formation of a new compound involves the elimination of hydroxyl group with substitution of quinolyl anion in catechol and *o*-cresol. The observed Arrhenius parameters are : E = 29.57 Kcals mole^{-1} and log A, sec^{-1} = 10.49, in catechol and in *o*-cresol, E = 33.40. Kcals mole^{-1} and log A sec^{-1} = 12.38. The normal pre-exponential factor, modest activation energy and tentative evidence of ions to the mechanism are viewed as supporting a bimolecular mechanism via an activated complex, comparison is made with that of picolinic acid in catechol.

IN the past, several kinetic studies have been reported on the decarboxylation of benzoic acid[1], oxalic acid[2], oxamic acid[3], oxanilic acid[4], malonic acid[5] and cinnamylidenemalonic acid[6] in the solvents resorcinol and catechol. The difference existing between picolinic acid[7] and quinaldinic acid is an additional benzene ring attached to it. It was expected that quinaldinic acid might follow the same mechanism as does picolinic acid in catechol. The picolinic acid decarboxylated in catechol in a manner analogous to malonic acid. Verhock[8] presented intermediate anion mechanism for the decarboxylation of various acids on the basis of kinetic investigations. However, no direct chemical evidence could be obtained for the occurrence of anions. The rapid reaction of the anions from dibromomalonic acid with bromine was reported by Pederson[9] and then later Muss[10]. Hall[11] found that mono-anion and the diacids have different rates of decomposition in aqueous solutions. We have reported in our earlier findings that mono-oxalate ion[12] and the free acid have different rates of decomposition in glycerine medium. The quinaldinic acid has never been the subject of kinetic study in catechol and *o*-cresol, it was found necessary to see whether it follows the same mechanism to that of picolinic acid or not. Kinetic evidence is pre ented for an ionic mechanism for the decarboxylation of quinaldinic acid in these solvents.

Experimental

Quinaldinic acid used in this investigation was prepared by the bromination of quinalidine in glacial acetic acid in the presence of sodium acetate, 2-tribromomethyl quinalidine was obtained and hydrolysis of the latter by boiling with dilute sulphuric acid yielded quinaldinic acid. Recrystallised the quinaldinic acid several times with glacial acetic acid. It melted at 156.3°, the reported m.p in the literature is 157°.

Catechol and *o*-cresol (BDH) analar grade, m.p = 105° and b. p = 191° respectively.

The kinetic experiments were conducted in a constant temperature oil-bath ± 0.05° as described in our previous articles[14,15]. In each set of experiments 0.3088 g sample of quinaldinic acid (the amount which was just required to produce 40.0 ml of CO_2 at NTP) was dropped in the usual manner into the reactor, containing 50 g catechol and 50 g catechol and 50 g *o*-cresol in separate runs.

Results

The decarboxylation was studied in catechol and *o*-cresol at the same temperatures for comparison of the results (Table 1). The plots of log $(V_\infty - V_t)$ vs t were linear in all the experiments indicating first order, where V_∞ is the maximum volume of CO_2 at the completion of the reaction and V_t is the volume at any time t. The average rate constants obtained from the slopes of the logarithmic plots are shown in Table 1. The plot of log k against reciprocal of the absolute temperature for each solvent resulted in straight lines. Energy of activation was calculated as $E = 2.303 \times R \times$ slope. The thermodynamic parameters were calculated using Eyring equation based upon the data are tabulated in Table 3 along with the data of picolinic acid. Table 2

TABLE 1—RATE-CONSTANTS FOR DECOMPOSITION OF QUINALDINIC ACID IN CATECHOL AND *o*-CRESOL.

Run temp. °C	No. of data pairs	Av. $k_1 \times 10^4$ (sec^{-1})	No. of data pairs	Av. $k_1 \times 10^5$ (sec^{-1})
		Catechol		*o-Cresol*
150	3	1.413	2	1.48
160	3	3.162	3	3.20
170	2	6.607	2	8.71
180	2	14.130	2	20.89

TABLE 2—EFFECT OF WATER ON THE RATE-CONSTANTS OF THE REACTION AT 180°C.

H_2O added	1 ml	2 ml	3 ml	4 ml
Catechol ($k_1 \times 10^5$) sec^{-1}	13.0	12.4	11.0	9.4
o-Cresol ($k_1 \times 10^5$) sec^{-1}	19.3	18.0	16.1	13.3

TABLE 3—COMPARISON OF ACTIVATION PARAMETERS

	E kcal/ mole	log A (sec^{-1})	$\Delta H^{\ne}$ kcals/ mole	$\Delta F^{\ne}$ kcals/ mole	$\Delta S^{\ne}$ cals/ mole/deg.
Catechol	29.57	10.49	28.69	34.67	−13.59
o-Cresol	33.40	12.38	32.52	34,52	− 4.61
Catechol[1] (Picolinic acid)	35.40	13.50	34.56	34.34	+ 2.50

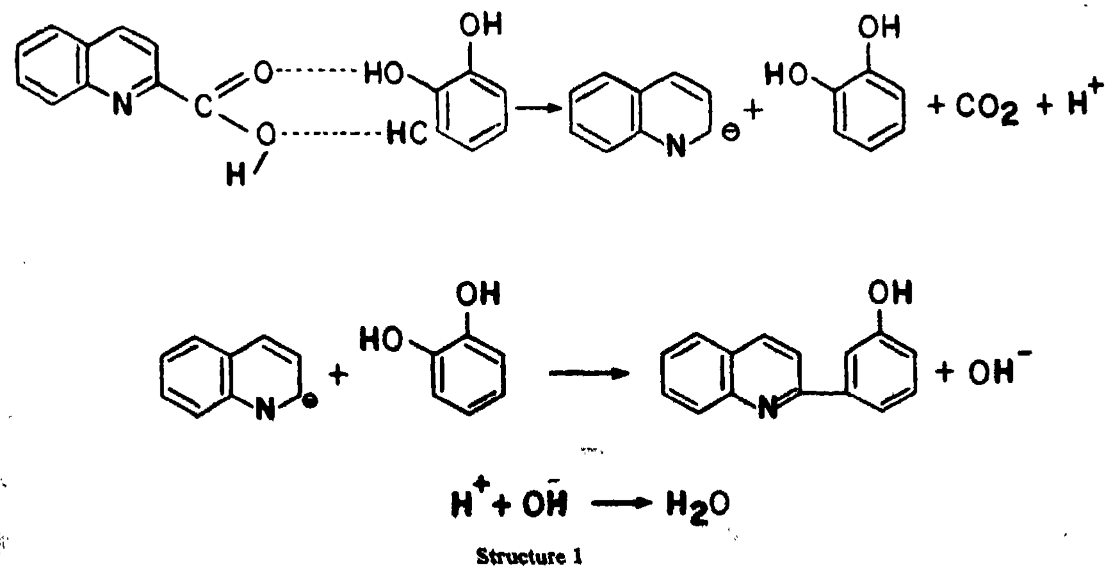
shows the decrease of rate constants by the addition of small amounts of water in the reactor with the solvents, when the reactor attained a constant required temperature, the acid was dropped. Water affected the rates quite considerably.

Discussion

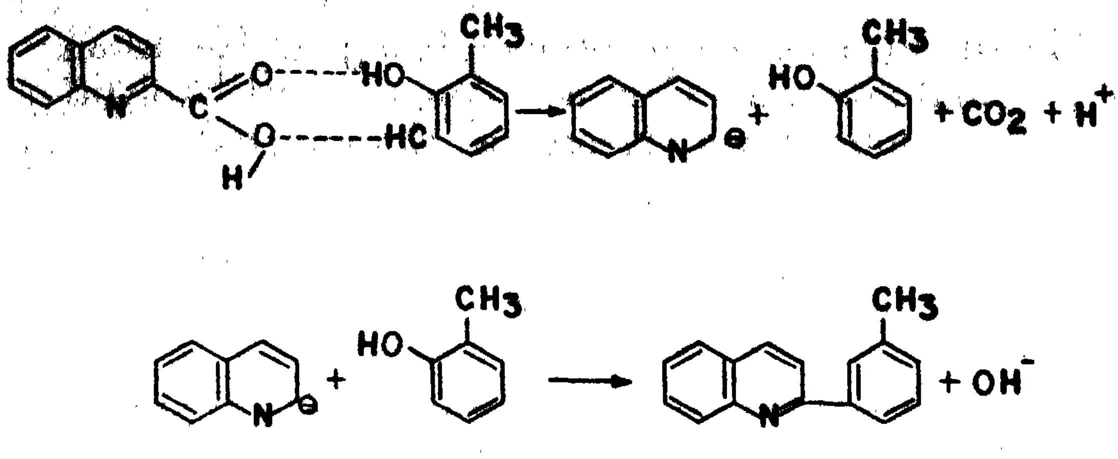
The decarboxylation of quinaldinic acid is kinetically first order similar to picolinic acid. The rate-determining step is an intermediate complex between the acid and the solvents analogous to several carboxylic acids[16,17]. The reaction mechanism may be presented in the following form :

The reaction (1) is slow and rate-determining step, the transition complex, yielded (the products) hydrogen ion, quinolyl anion and carbon dioxide. However in the second step the quinolyl anion and the solvent might be combining to form phenyl quinoline displacing OH^- from the adjacent position in catechol. Hence the rapid addition/substitution might be taking place. The displaced OH^- ion forms water combining with H^+, from the reaction (1). The rapid reactions of step (2) and (3) might be affecting the velocity of a reaction for the decomposition of the acid. For comparison, a similar solvent in which methyl and hydroxyl groups are adjacent was selected to study the reaction mechanism. In *o*-cresol, rates are relatively faster than that of catechol, possibly the isolated methyl group of the solvent having more accelerative effect than that of the isolated hydroxyl group of catechol[18,19]. However, the relatively low activation energy for a reaction is related to the effective negative charge on the solute causing an increase in the attraction between the solvent and quinolyl anion. The H^+ and OH^- ions are also partly responsible in lowering the energy of activation in comparison to picolinic acid. Hence higher rates and higher energy of activation for picolinic acid in catechol. Apart from this, the intermediate complex of picolinic acid in the solvent catechol is smaller in size than that of quinaldinic acid in catechol. Hence bulkier the complex, slower the rate and more stable the complex and more negative the entropy of activation. Picolinic acid gave positive entropy of activation whereas quinalidinic acid showed negative entropy of activation (Table 3). The lowering of $\Delta S^{\ne}$ is undoubtedly attributable to the fact that extensive association is obtained between solvent and quinolyl anion OH^- and H^+ ions and undissociated molecules of catechol.

Picolinic acid is a stronger acid than quinaldinic acid. One would predict, therefore that $\Delta H^{\ne}$ would be larger for picolinic acid- The high steric factor and high value of enthalpy of activation are in accordance



Structure 1



$$H^+ + OH^- \longrightarrow H_2O$$

Structure 2

without predictions for picolinic acid. Hence, there would be less steric hindrance in the formation of activated complex. The added water of the reaction showed that the reaction velocity is retarded in both the solvents of this investigation (Table 2). This indicates that the decarboxylation reaction is suppressed by the addition of water. The water molecule probably adds across the carbonyl double bond of the activated complex and stabilizes the complex. The reaction mechanism in catechol and *o*-cresol is similar and is shown above.

In this reaction the end products are methyl-phenyl quinoline and water and in reaction (1) phenyl quinoline and water. It was expected that H^+ ions might be accelerating the rates but the fast reaction of $(H^+ + OH^-)$ could not effect on the rate. However this is beyond expectation.

The first order kinetics and the simplicity of the stochiometry between 150 – 180° interpretation of the findings is thus limited. We believe the results at hand lend mild support to the assumption of ionic decomposition mechanism through the formation of activated complex. The direct hydrogen transfer to carbon in the benzene ring occurs due to the formation of C – C bond between solvents and quinolyl anion but the entropy of activation would seem to be somewhat high for the formation of three benzene rings. The formation of methylphenyl quinoline, phenylquinoline involve the elimination of hydroxyl group with substitution by quinolyl anion in the adjacent position. Similar displacements in an adjacent position have been studied by Gilman and coworkers[20] who however reported no mechanism.

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Measurements of Concentration Range of Nernstian Response of Some Common Anions in Electrolytic Solutions with 'Neosepta' Membranes*

S. K. SAHARAY and A. S. BASU

Department of Chemistry, University of Burdwan, Burdwan, West Bengal, India

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The concentration ranges of Nernstian response of some common anions, Cl^-, Br^-, I^-, NO_3^-, BrO_3^-, IO_3^- and SO_4^{2-} were studied singly in electrolyte solutions with three anion exchange membranes AV-3, AV-3T and AVS-3T of the 'Neosepta' family as electrodes. Membranes show more or less good permselectivity within a certain range of concentrations (narrower for NO_3^-, BrO_3^-, IO_3^- and SO_4^{2-} ions) so long these are not widely different on the two sides. When the concentration differences are larger, greater deviations take place. It is obvious from the deviation pattern that the hydrated ionic size plays a very important role in the water transport which seems to be the major cause of deviation.

THE potentiometric determination of the activities of anions by membrane electrodes is now a well established method[1-5]. Recently 'selective anion sensitive membrane electrodes' to respond to any particular anion have been developed as 'a new technology'[6-9].

The purpose of the present investigations is to study the electrode behaviour of some anion exchange membranes of the 'Neosepta' family prepared by Mizutani et al[10] to measure the anion activities in electrolytic solutions with a view to the future possibility of utilising the 'base membranes' as ionselective electrodes by introducing functional groups specific for any particular ion.

For the establishment of an ion-exchange membrane as a suitable electrode for the determination of ionic activities, it is necessary to study the concentration ranges over which the membrane retains its permselectivity and hence obeys the Nernst equation. Conventionally, the following cell was set up

$$\underset{(S)}{Hg/Hg_2Cl_2}, \ \underset{(satd.)}{KCl}/\underset{a_1}{Solution}/Membrane/\underset{a_2}{Solution}/\underset{(satd.)}{KCl}, \ \underset{(S)}{Hg_2Cl_2/Hg}$$

The theoretical values of the e.m.f.s were calculated using the well known Nernst equation for concentration potential.

Experimental

The three anion exchange membranes AV-3, AV-3T and AVS-3T were used in this study. The setting up of the electrodes for the measurements were done by the usual procedure of the early workers (loc. cit).

Standard solutions of the anions studied were prepared with A.R. or G.R. quality potassium salts, dried properly for removing adsorbed moisture. With regard to ionic activities the arbitrary non-thermodynamic assumptions of single ion activity[11,12] were accepted, and the standard solutions of desired activity values were so prepared after calculation of the activity co-efficients by graphical interpolation method that a constant ratio, viz. 1:3 was maintained between two successive solutions, which helps in the understanding of the deviation pattern.

The e.m.f.s were read within ± 0.1 mv. with the help of a Cambridge Potentiometer with a suspended coil galvanometer having a current sensitivity of 10^{-10} ams/mm/m. All measurements were taken at the room temperature, $25 \pm 1.0°$. Membranes, at least, from the three different portions of the large sheets were tested for the uniformity and the results were found to be reproducible within 1%. The steady potential was recorded after the frequent renewal of the two solutions on both sides of the membrane. The membranes were initially tested for asymmetry potential, and those showing almost zero or negligible asymmetry potential were used for the present investigations. In order to avoid any error due to the development of asymmetry during the measurement, average of at least six readings differing not more than ± 0.5 mv. were recorded. Measurements were also taken by changing inside solution out and outside solution in to check any asymmetry developed during the experiments.

Results and Discussions

The studies of the concentration potentials of the anions Cl^-, Br^-, I^-, NO_3^-, BrO_3^-, IO_3^- and $SO_4^{=}$ are performed with three anion-exchangers AV-3, AV-3T and AVS-3T. From the potential data obtained the concentration range of Nernstian response or ideal

* Membranes received as gift samples from Dr. Y. Mizutani, Tokuyama Soda Company, Japan.

permselectivity is established. The range of concentrations over which these three membranes register reasonably satisfactory results at 1:3 ratio are shown in table 1 and represented graphically (fig. 1 and 2) with a typical membrane AVS-3T.

TABLE 1—THE VALID RANGE OF ACTIVITIES OF NERNSTIAN RESPONSE FOR THE THREE DIFFERENT MEMBRANES AT THE 3 : 1 RATIO OF MEASUREMENT.

Ions	Activity Range
Cl^-	0.1×10^{-3} – 72.9×10^{-3}
Br^-	0.1×10^{-3} – 72.9×10^{-3}
I^-	0.1×10^{-3} – 72.9×10^{-3}
NO_3^-	0.1×10^{-3} – 72.9×10^{-3}
BrO_3^-	0.1×10^{-3} – 24.3×10^{-3}
IO_3^-	0.1×10^{-3} – 24.3×10^{-3}
SO_4^{--}	0.1×10^{-3} – 8.1×10^{-3}

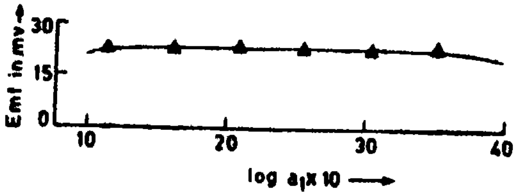


Fig. 1. Range of Nernstian response of AVS-3T membrane for Cl^- ; Br^- and I^- at 3 : 1 ratio O – Cl^- ; △ – Br^- × – I^-.

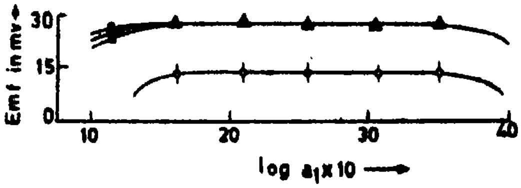


Fig. 2. Range of Nernstian response of AVS-3T membrane for univalent and bivalent ions at 3 : 1 ratio O – NO_3^- ; △ – BrO_3^- ; × – IO_3^- ; ϕ – SO_4^{--}

The range of the bivalent ion SO_4^{--} (vide figure 2 and Table 1) is much lower than that of monovalent ion, Cl^-, Br^- and I^-. This may be due to the reduction in the membrane charge by adsorption of opposite ions on the surface[2,13]. In case of monovalent anions the concentration range over which the Nernst potential is obeyed is more or less the same for Cl^-, Br^- and I^- ions, except at higher activity range between 24.3×10^{-3} to 72.9×10^{-3} where the following sequence is obeyed, $I^- > Br^- > Cl^-$. This may be due to the increase in the membrane charge in case of iodide ion by any adsorptive effect besides the coulombic binding and this possibility has been discussed in an excellent manner by Gregor[14]. Much lower range in case of BrO_3^- and IO_3^- ions may well be explained by the substantial increase in the pore volume by these large hydrated ions and hence the reduction in the membrane charge (loc.cit) which enhances the co-ion transfer particularly the mobile ion like K^+, at higher concentration.

From the viewpoint of TMS equation the major cause of the difference between the actual membrane potential values and those of theoreticals at higher concentration of electrolytes irrespective of mono- and bi-valent ions. is due to gross changes of the transport numbers within the membranes owing to co-ion transport and thus failing of the Donnan exclusion phenomena. Though the deviations at the dilute ranges are not too easy to explain but one may seek for the cause in the phenomena of membrane hydrolysis suggested by Scatchard[15]. If the transport number is calculated from the membrane potential data it is seen that t_- of any anion is nowhere equal to unity throughout the range studied. This occurs even in case of any ideally permselective membrane, which may be due to water transport. A more important factor which has been ignored in the TMS equation is the difference of solvent (water) activities on the two sides of the membrane and hence the influence of water transfer has been neglected.

From the detailed discussion regarding the water transport mentioned by earlier workers[16-18], it is presumed that greater the difference in water activities on the two sides of the membrane, the larger will be the deviation due to water transport particularly with the membranes having less flow resistance[19]. With a view to this idea the concentration potentials have also been measured in a different way.

The e.m.f.s are measured by interposing the membranes between the same standard solutions, where the activity of an ion on one side of the membrane is kept fixed and the activity of that on the other side is changed so that the ratio gradually increases viz. 1:9, 1:27, 1:81 and so on but the upper and the lower limits are always within the range of Nernstian response as observed from the earlier measurements with fixed activity ratio 1:3. The graphical representations should yield straight lines passing through the origin having slope values in ideal cases either 59.0 mv. in case of univalent or 29.5 mv. in case of bivalent ions. Figures 3 and 4 represent the observations (shown by the symbols), where e. m. f. s are plotted against log $\frac{a_1}{a_2}$ keeping a_2 constant with a typical membrane AVS-3T. The presumption of water transport seems to be justified by the deviations from the theoretical slope values observed with increase in the a_1/a_2 ratio.

The theoretical (shown by the dotted lines) and experimental values almost coincide upto certain range and afterwards the deviations start which indicate that as the concentration or activity on the two sides of the membranes differs widely the amount of deviation from ideal behaviour increases more and more. Though the nature of deviations in all cases are the same but their magnitudes vary depending on the nature of the ion.

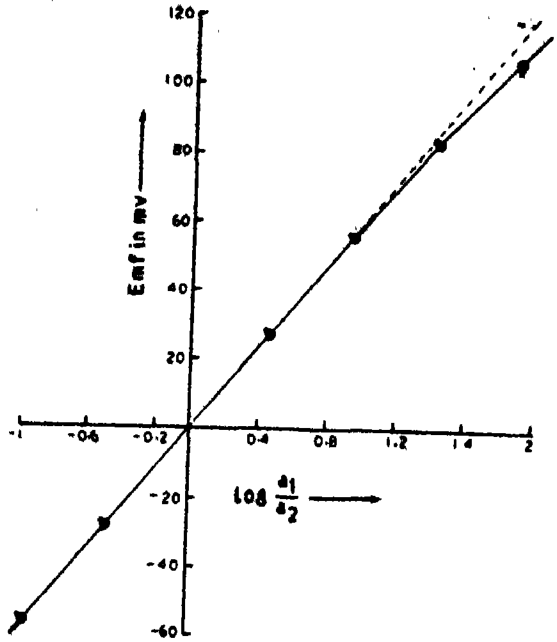


Fig. 3. Experimental results with AVS-3T membrane (shown by symbols) showing the deviation pattern from the theoritical values when the activity ratio gradually increases. O – I^- ; △ – Br^- ; × – Cl^-.

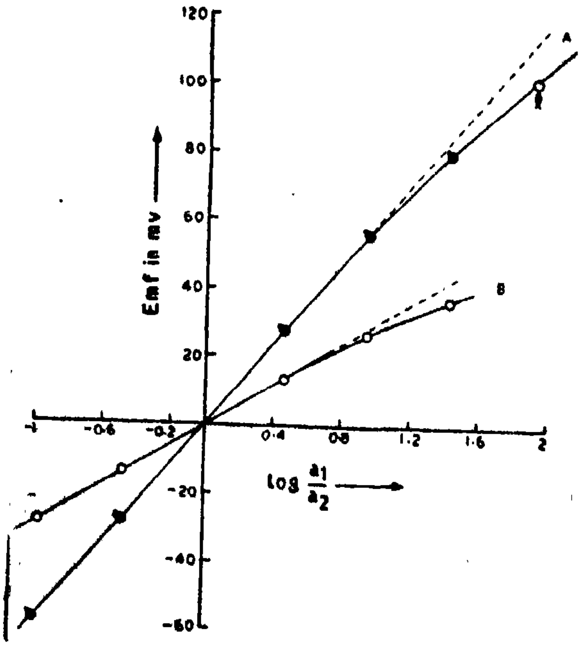


Fig. 4. Experimental results with AVS-3T membrane (shown by symbols) of univalent and bivalent ions showing the deviation pattern from the theoretical values when the activity ratio gradually increases.
A – univalent O – NO_3^- ; △ – BrO_3^- ; × – IO_3^-
B – bivalent O – SO_4^{--}

The percent deviations are also shown in table 2 in connection with AVS-3T membrane.

TABLE 2—THE PERCENT DEVIATION FROM THE IDEAL VALUES WITH INCREASE IN THE ACTIVITY RATIO SHOWN WITH A TYPICAL MEMBRANE AVS-3T. THE FIXED ACTIVITY ON ONE SIDE OF THE MEMBRANE IS 0.0009.

Ions	Activity Ratio			
	3 : 1 (%)	9 : 1 (%)	27 : 1 (%)	81 : 1 (%)
Cl^-	<3.0	<3.0	3.4	8.8
Br^-	<3.0	<3.0	<3.0	6.9
I^-	<3.0	<3.0	<3.0	6.0
NO_3^-	<3.0	<3.0	5.0	10.0
BrO_3^-	<3.0	<3.0	6.4	12.8
IO_3^-	<3.0	<3.0	7.0	14.8
SO_4^{--}	<3.0	4.3	14.2	–

From the table 2 it may be pointed out that

(i) The increase in percent deviation from ideal permselectivity is very much gradual with the increase in the concentration difference on the two sides of the membrane.

(ii) The pattern of percent deviation follows a parallel order with the hydrated ionic size of the ions concerned.

Regarding the ions I^-, Br^- and Cl^- the deviations, upto the ratio 1:27, are more or less the same throughout i.e. within the limits of error of the Nernstian response of the membranes. But for the larger ions like NO_3^-, BrO_3^- and IO_3^- (though univalent) and the higher valent ion like $SO_4^=$ the ratio upto which the membranes give the same Nernstian response is 1:9 after which the response is otherwise. The percent deviations follow the sequence

$$I^- < Br^- < Cl^- < NO_3^- < BrO_3^- < IO_3^- < SO_4^=$$

which is more or less the same as that of hydrated ionic size.

This suggests that the hydrated ionic size of the ion plays a very important role in the water transport which seems to be the major cause for this deviation.

Also there may be other possibilities like osmotic degradation[16] due to wide difference of water activities on the two sides. But it may be said that the effect, if any, seemed to be very negligible since the equilibrium was established very repidly during the measurements and the results were reproducible within ± 0.2 mv. The development of asymmetry potential on the membrane surface and/or on the KCl-agar tips is also possible, but these effects were tried to be nullified, as far as practicable, by interchanging the solutions on the two sides and the mean values were noted within ± 0.5 mv.

From all these observations it is quite evident that these "Neosepta" like membranes offer a more or less good permselectivity in the Nernstian response within a certain range of concentration of electrolytes. Their response is otherwise within the same range as the concentrations on the two sides of the membrane differ widely, particularly for the ions having larger hydrated ionic sizes though the permselectivity is maintained. The special advantages of these membranes are due to the fact that these are suitable to handle, attain rapid equilibrium and have higher operative life.

Finally, it may be mentioned as Gregor[1] has pointed out, that in order to establish a membrane electrode for its Nernstian response over a concentration range, it is always preferable to make use of more than one method, specially for the membranes having low electrical resistance.

Acknowledgement

The authors are indebted to Dr. Y. Mizutani, Tokuyama Soda Company. Japan, for the gift samples of the membranes. They also thank the University of Burdwan for a Research Fellowship to one of the authors (S.K.S) and Prof. S K. Siddhanta, Head of the Dept. of Chemistry, for providing necessary facilities.

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Synthesis of Possible Antifertility Compounds. Synthesis of *Bis* and *Di* Derivatives of Coumarins

VINAY S. MISRA and (Km) SHAKUNTALA AGARWAL

Department of Chemistry, Lucknow University, Lucknow

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Several new *bis* and *di* (7 or 4-coumarinyloxy) alkanes have been prepared as possible antifertility agents. The structure has been ascertained by their elemental analysis and the mass spectra of one representative *bis*-coumarin.

MAJORITY of neutral coumarins show appreciable estrogenic activity which is due to the oxygen atom in heterocyclic ring and a *p*-OH group in the 2-aroyl substituent. Recently Lednicer et al[2] prepared a number of 3, 4 diaryl coumarins, sterically related to 1, 2-diarylindene and showed that some of them possess antifertility activity presumably due to their estrogenic activity and they also exhibited antiimplantation activity in rats.

Marked antifertility activity has been observed in compounds incorporating a triarylethylene or ethane pattern and also in 3, 4-diphenyl, 1,2,3,4-tetrahydronapthalene when the alkoxy group[3-6] was introduced in the nucleus of former and halogen[7-9] substituent is incorporated in the phenyl rings of the latter. Recently some alkoxy and halogen substituted 3,4-diarylcoumarins with a possible antifertility interest were also synthesised by Tiwari and Kumar[10].

In view of these observations the present authors prepared several additional analogues of neutral bis (I) and dicoumarins (II) with methyl, ethyl, acetyl and chloro substituents in the rings.

7-Hydroxycoumarins were prepared by adopting the procedure of Pechman[11]. 7-hydroxy, 4-methyl and 6-substituted coumarins were obtained by using the method of Chakravarti and Ghosh[12] and 4-hydroxy coumarin was synthesised by using the procedure of J. Boyd and A. Robertson[13]. Thus in all eleven new compounds were sythesised. The analytical data are given in Tables 1 and 2.

Bioassay

Anti-implantation activity: The *in vivo* anti-implantation activity of all the eleven compounds was studied on adult albino proven female and male rats.

In this preliminary screening female rats were treated with the drug at a dose of 20 mg/Kg. Four such rats, constituted a group and a female : male ratio of 4 : 1 was maintained. The compounds, under test, were suspended in a mixture of gum acacia and distilled water. The suspension was fed orally from day 1 to 5 post-coitum. The day in which the sperms were seen in the vaginal smears was taken as the day 1 of the pregnancy. The animals were laprotomized on the 10th day of the pregnancy and the number of implantations in each case was noted. However, none of the compounds was found active at this dose.

Anti-estrogenic activity of these compounds is at present in progress and the results will be published later.

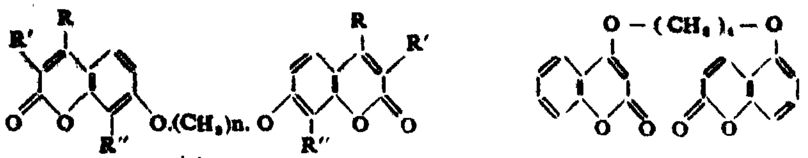
Experimental

1. Bis-*(7 or 4-coumarinyloxy) alkanes*: An appropriate hydroxycoumarin (.025 mole) and a dibromoalkane (.01 mole) were refluxed together in dry acetone (80 ml.) and anhydrous potassium carbonate (8 g.) for 36 hours till a negative ferric chloride test was observed. The reaction mixture was filtered while hot and the resultant precipitate washed first with 10% NaOH solution and then with water. The solid thus obtained was recrystallised from D. M. F.-water mixture.

2. Di-(*7 or 4-coumarinyloxy*) *alkanes :* A mixture of two different coumarins (1 : 1) and dibromo alkane (0.1 mole) were refluxed in dry acetone and anhydrous potassium carbonate (0.2 mole) for 36 hours and the resultant product was isolated as in the previous case.

Mass Spectrum : As the compounds were insoluble in solvents generally used in N. M. R. spectroscopy and comparable I.R. data are not available, mass spectra of one of the *bis*-coumarins, i.e. compound No. 4 of Table I was determined. The mass spectra confirms the mol. weight of the *bis*-coumarin (M^+ 392).

TABLE 1

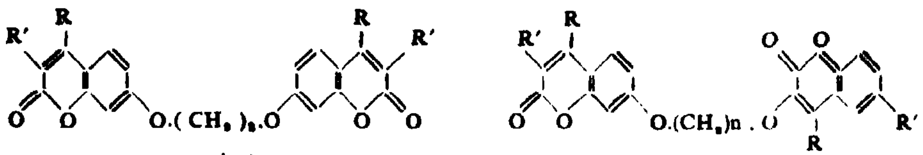


(a) (b)

(I)

Sl. No.	R	R′	R″	N	m. p*. °C	Mol. formula	Calculated C%	Calculated H%	Found C%	Found H%
Series a										
1	–H	–H	–H	2	250	$C_{20}H_{14}O_6$	68.56	4.00	68.02	3.99
2	–CH_3	–H	–H	2	227	$C_{22}H_{18}O_6$	69.84	4.76	69.94	4.71
3	–H	–H	–H	3	160	$C_{21}H_{16}O_6$	69.23	4.12	68.99	4.25
4	–H	–H	–H	3	189	$C_{23}H_{20}O_6$	70.40	5.10	70.90	5.36
5	–H	–Cl	–H	3	120	$C_{26}H_{18}O_6Cl_2$	59.86	4.12	59.41	4.32
6	–H	–H	–CoCH	3	212	$C_{27}H_{24}O_8$	68.03	4.91	67.89	4.58
Series b										
7	–	–	–	3	181	$C_{21}H_{16}O_6$	69.23	4.39	69.51	4.62

TABLE 2



(c) (d)

(II)

Sl. No.	R	R	n	m. p*. °C	Mol. formula	Calculated C%	Calculated H%	Found C%	Found H%
Series c									
1	–CH_3, –H	–H	3	162	$C_{22}H_{18}O_6$	69.84	4.76	69.25	4.28
2	–CH_3, –CH_3	–C_2H_5, –H	3	150	$C_{25}H_{24}O_6$	71.19	5.71	71.38	5.99
Series d									
3	–CH_3	–H	3	158	$C_{22}H_{18}O_6$	69.84	4.76	69.53	4.59
4	–H	–H	2	225	$C_{20}H_{14}O_6$	68.33	4.00	68.57	3.91

* All melting points are uncorrected and were taken in open capillary tubes.

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Organophosphoryl Ethanolamine Analogues III. Synthesis of N, N-Dimethylphosphoramidic Acid Esters

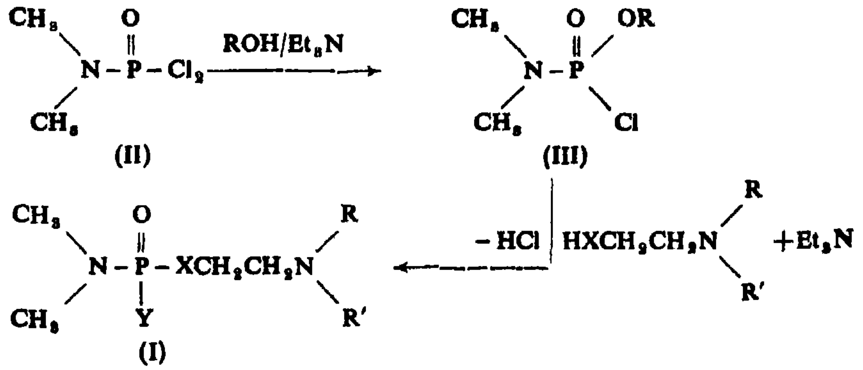
M. EL-DEEK, A. A. EL-MEHY and M. AMER

Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, A. R. E.

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A series of phosphoramidic acid esters having the general structure (I) has been prepared as potential anticholinestrases agents. In this series X equals O or S. The compounds were prepared in a single vessel, in good yield.

THE anticholinestrases are widely used in medicine[1] and in agriculture as insecticides[2-6]. The most toxic derivatives are used as warfare agents[7]. In the course of our studies on the synthesis of organophosphates acting as anticholinestrases by irreversible inactivity of the enzyme cholinestrase[8], it was of interest to determine how various substituents on the phosphorus atom affect the electrophilicity of the phosphoryl group which would in turn affect the physiological activity. This paper describes the synthesis of the phosphoramidic acid esters (I), by a very simple method involving the condensation of phosphoramidic dichloride (II) with alcohols, to give the chlorides (III), the latter in turn was treated *in situ* with 2-tertiary-aminoethanol to yield (I). This is shown in the following scheme :



X = O or S. Y = alkoxy group.

The infrared spectra of all the compounds were recorded as thin films, using a sodium chloride window on a spectromom 2000 infrared spectrometer. The infrared data indicated that all the compounds exhibit a sharp band around 1300 cm^{-1}, (P=O), and two bands at about 1020 and 770 cm^{-1} due to the asymmetric and symmetric stretching vibration of the P–N–C group respectively. However, the 1020 cm^{-1} band may be due to P–O–C (alkyl).[9]

Because of their expected physiological properties, a study for their biological effects will be made and the results will be reported in due time.

Experimental

General procedure for the preparation of phosphoramidic acid esters (1-16) :

A mixture of 0.1 mol of the appropriate alcohol and 0.1 mol of triethylamine in 200 ml dry benzene was placed in a 500 ml round bottomed, three-necked flask fitted with a mechanical stirrer, dropping funnel and a condenser. The mixture was cooled down to 5-10°. To the cold mixture 0.1 mol of N,N-dimethylaminophosphoramidic dichloride dissolved in 100 ml dry benzene was added with stirring at such a rate keeping the reaction temperature below 10°. A white precipitate of triethylamine hydrochloride was separated during the addition. The reaction mixture was stirred at room temperature for another 2 hours. To this a mixture, 0.1 mol of 2-tertiaryaminoethanol or thioethanol and 0.1 mol of triethylamine in 100 ml dry benzene was added dropwise with stirring. Upon completion of the addition the temperature was gradually raised. Heating and stirring was continued for further 3 hours, keeping the temperature between 60-70°. This mixture was allowed to cool at room temperature. Triethylamine hydrochloride, separated as white precipitate, was filtered and washed with 100 ml of dry benzene. The solvent was then removed and the residue was distilled under vacuum. The physical data are summarized in table 1.

TABLE 1—$(CH_3)_2N-P(=O)(Y)-X-CH_2CH_2N(R)(R')$

No.	X	Y	R	R′	b. p. °C/mm. Hg	n_D^{20}	d_4^{20}	Molecular formula	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
1	O	Y_1	$-C_2H_5$	$-C_2H_5$	97-98/5	1.4342	0.8390	$C_9H_{23}N_2O_3P$	45.37	9.73	11.76	45.29	9.63	11.23
2	O	Y_1	$-C_3H_7(n)$	$-C_3H_7(n)$	63/0.6	1.4315	0.8372	$C_{11}H_{27}N_2O_3P$	49.61	10.22	10.52	49.62	10.09	10.50
3	O	Y_1	$-CH_3$	$-C_6H_5$	97-99/0.4	1.5160	0.9741	$C_{12}H_{21}N_2O_3P$	52.93	7.77	10.29	52.87	7.73	10.32
4	O	Y_2	$-C_2H_5$	$-C_2H_5$	85-86/3	1.4287	0.8381	$C_{10}H_{25}N_2O_3P$	47.61	9.99	11.10	47.55	9.92	10.87
5	O	Y_2	$-C_3H_7(n)$	$-C_3H_7(n)$	92-93/5	1.4330	0.8572	$C_{12}H_{29}N_2O_3P$	51.41	10.43	9.99	51.38	10.08	9.88
6	O	Y_2	$-CH_3$	$-C_6H_5$	128/4	1.4978	0.9921	$C_{13}H_{23}N_2O_3P$	54.54	8.1	9.78	54.51	8.12	9.63
7	O	Y_3	$-C_2H_5$	$-C_2H_5$	62-63/1.4	1.4357	0.8142	$C_{11}H_{27}N_2O_3P$	49.61	10.22	10.52	49.57	10.20	10.49
8	O	Y_3	$-C_3H_7(n)$	$-C_3H_7(n)$	53-55/0.6	1.4290	0.8605	$C_{13}H_{31}N_2O_3P$	53.04	10.61	9.52	53.18	10.54	9.51
9	O	Y_3	$-CH_3$	$-C_6H_5$	108-110/2	1.4560	1.1320	$C_{14}H_{25}N_2O_3P$	55.99	8.39	9.33	55.87	8.32	9.33
10	O	Y_4	$-C_2H_5$	$-C_2H_5$	90-91/10	1.4532	0.9371	$C_{11}H_{25}N_2O_3P$	50.00	9.53	10.60	49.87	9.54	10.62
11	O	Y_4	$-C_3H_7(n)$	$-C_3H_7(n)$	102-103/10	1.4462	0.9284	$C_{13}H_{29}N_2O_3P$	53.41	10.00	9.58	53.37	9.98	9.55
12	O	Y_4	$-CH_3$	$-C_6H_5$	122-123/5	1.5344	1.1514	$C_{14}H_{23}N_2O_3P$	56.37	7.77	9.39	56.21	7.69	9.37
13	S	Y_1	$-C_2H_5$	$-C_2H_5$	110-112/3	1.4585	0.9838	$C_9H_{23}N_2O_2PS$	42.50	9.12	11.01	42.52	9.11	11.00
14	S	Y_2	$-C_2H_5$	$-C_2H_5$	82-83/1	1.4735	0.8482	$C_{10}H_{25}N_2O_2PS$	44.76	9.39	10.44	45.74	9.37	10.42
15	S	Y_3	$-C_2H_5$	$-C_2H_5$	68-70/0.2	1.4560	0.9545	$C_{11}H_{27}N_2O_2PS$	46.79	9.64	9.92	46.82	9.69	9.91
16	S	Y_4	$-C_2H_5$	$-C_2H_5$	87-88/1	1.4621	0.9371	$C_{11}H_{25}N_2O_2PS$	47.12	8.99	9.99	47.20	8.98	9.97

$Y_1 = -OCH_3$; $Y_2 = -OC_2H_5$; $Y_3 = -C_3H_7$ (iso); $Y_4 = -OCH_2-CH=CH_2$.

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Solute-Solvent Interactions in Solutions of Sodium Formate in Water and Aqueous Ethyl Formate

R. L. BLOKHRA and P. C. VERMA

Chemistry Department, Himachal Pradesh University, Simla-171 005

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Solute-solvent interaction in solutions of sodium formate in water and aqueous ethyl formate (5% by weight) has been deduced from the values of the limiting apparent molar volume, ϕ°_{v}, the B-coefficient of the Jones-Dole equation and from conductance studies at different concentrations and at different temperatures. It is found that the salt behaves as structure breaker in water and as structure promotor in case of aqueous ethyl formate.

SOLUTE-solvent interaction studies have been a subject of interest among physical chemists for the last two decades[1-6]. The inference regarding the interactions is derived either from molar volume studies or viscosity studies or conductance studies or from all these properties[7,8] together. Literature is full of such studies in pure solvents but investigations in mixed solvents are scanty. The studies in mixed solvents have never been undertaken in solutions where there is a similarity in ions of the salt and the solvent molecules. The present work was undertaken with the object of knowing the nature of solute-solvent interactions in such system from the molar volume, viscous flow and conductance data of sodium formate in water and aqueous ethyl formate. Sodium formate has been found to have negligible solubility in the formate and we carried out measurements in aqueous ethyl formate having water content enough to have solution of sufficient concentration in the salt.

Experimental

Sodium formate was used after usual purification[9]. Ethyl formate was dried over CaO and was distilled before use. The specific conductance, viscosity, density of ethyl formate at 25° is 3.4×10^{-7} ohm^{-1} cm^{-1}, 0.00363 P and 0.91561 $g.ml^{-1}$ respectively. These are in good agreement with the literature values[10]. Water of conductivity 10^{-6} $ohm^{-1}cm^{-1}$ was used for making aqueous solutions and 5% (by weight) of aqueous ethyl formate. All solutions of the electrolytes were prepared by weight and the conversion of the molality into molarity was carried out by the expression given elsewhere[11]. The density measurements, viscosity measurements and conductance measurements were carried out by the method described earlier[11-13]. All measurements except of viscosity were made in the water bath which was placed in an air thermostat having fluctuations always below 0.02°. In case of viscosity, measurements were carried out in air thermostat having temperature fluctuations of the order 0.05°.

Results and Discussion

The apparent molar volume, ϕ_v, is calculated from the density data by using the equation[14]

$$\phi_v = \frac{1000\,(d_0 - d)}{m\,d\,d_0} + \frac{M_2}{d} \quad \ldots \quad (1)$$

where ϕ_v represents the molar volume of the electrolyte, d the density of the solution, d_0 the density of the solvent, m the molality of the solution and M_2 the molecular weight of the electrolyte. The density d, apparent molar volume ϕ_v, viscosity and the equivalent conductance Λ of the solutions at different concentrations for different systems are given in Table 1.

The density of the solutions can be represented by Root's equation[15] :

$$\frac{d - d_0}{C} = A - B\sqrt{C} \quad \ldots \quad (2)$$

where A and B are the constants of the Root's equation. On plotting $d\text{-}d_0/C$ versus $\sqrt{C}$, a straight line should be obtained and we get straight line in each case. Values of A and B evaluated from the intercept and slope of the plots are given in Table 2.

The apparent molar volume has been found to vary linearly with the square root of the concentration and the data can be represented by the relation[16] :

$$\phi_v = \phi_v^0 + S\sqrt{C} \quad \ldots \quad (3)$$

where ϕ_v^0 is the limiting apparent molar volume, and S is the experimental slope. Here ϕ_v^0 is a measure of solute-solvent interaction and for different systems the limiting apparent molar volume for sodium formate are given in Table 3.

TABLE 1—DENSITY, APPARENT MOLAR VOLUME, VISCOSITY AND EQUIVALENT CONDUCTANCE OF SODIUM FORMATE IN WATER AND 5% AQUEOUS ETHYL FORMATE.

Concentration C (mol. l^{-1})	Density d (g. ml^{-1})	Apparent molar volume ϕ_v (ml. $mole^{-1}$)	Viscosity η (cp)	Equivalent conductance Λ ($ohm^{-1}cm^{2}$)
		In Water		
	Temperature : 30°C,	$d_0 = 0.99567$ g. ml^{-1},	$\Lambda_0 = 150.90$ $ohm^{-1}cm^2$	
0.00248	—	—	—	140.01
0.00869	—	—	—	127.02
0.01379	—	—	—	119.10
0.02105	—	—	—	115.02
0.03248	0.99706	25.32	0.805	109.14
0.06445	0.99841	25.62	0.810	101.95
0.12156	1.00078	25.81	0.817	95.31
0.18063	1.00322	26.33	0.827	—
0.23713	1.00533	26.54	0.835	—
0.33074	1.00929	26.95	0.848	—
0.42267	1.01293	27.31	0.863	—
	Temperature : 35°C,	$d_0 = 0.99406$ g. ml^{-1},	$\Lambda_0 = 166.50$ $ohm^{-1}cm^2$	
0.00302	—	—	—	154.02
0.00753	—	—	—	143.43
0.01405	—	—	—	135.43
0.01963	—	—	—	129.53
3.02957	0.99541	22.49	0.723	122.81
3.05486	0.99653	23.10	0.725	111.89
0.09872	0.99845	23.50	0.728	105.97
0.15603	1.00094	24.06	0.732	—
0.22238	1.00374	24.46	0.739	—
0.31933	1.00776	25.25	0.750	—
0.41469	1.01163	25.80	0.784	—

(Contd.)

(TABLE 1 CONTD.)

Concentration C (mol. l^{-1})	Density d (g. ml^{-1})	Apparent molar volume ϕ_v (ml. $mole^{-1}$)	Viscosity η (cp)	Equivalent conductance Λ ($ohm^{-1}cm^{-2}$)
Temperature : 40°C,	d_0 = 0.99224 g. ml^{-1},	Λ_0 = 178.70 $ohm^{-1}cm^2$		
0.00301	—	—	—	164.12
0.00726	—	—	—	152.51
0.01383	—	—	—	143.75
0.02406	—	—	—	134.10
0.03821	0.99403	21.32	0.657	124.45
0.06827	0.99538	22.15	0.667	116.51
0.11371	0.99739	22.87	0.672	107.97
0.16605	0.99957	24.05	0.678	—
0.23423	1.00243	24.69	0.687	—
0.33756	1.00646	26.09	0.698	—
0.44493	1.01084	26.41	0.715	—
In 5% Aqueous Ethyl Formate				
Temperature : 30°C,	d_0 = 0.99574 g. ml^{-1},	Λ_0 = 138.70 $ohm^{-1}cm^2$		
0.00422	—	—	—	130.00
0.01716	—	—	—	121.00
0.03705	0.99785	11.12	0.903	—
0.03811	—	—	—	114.77
0.05336	—	—	—	107.00
0.08061	1.00011	13.89	0.926	97.47
0.11902	—	—	—	91.00
0.14220	1.00283	18.23	0.936	83.16
0.19802	1.00534	19.61	0.951	—
0.25713	1.00711	23 90	0.956	—
0.33756	1.01062	24.03	0.975	—
0.45661	1.01512	25.68	0.999	—

(Cont.)

(TABLE 1 CONTD.)

Concentration C (mol. l^{-1})	Density d (g. ml^{-1})	Apparent molar volume ϕ_v (ml. $mole^{-1}$)	Viscosity η (cp)	Equivalent conductance Λ ($ohm^{-1}cm^{-2}$)
Temperature : 35°C,	d_0=0.99427 g. ml^{-1},	Λ_0=156.90 $ohm^{-1}cm^2$		
0.00491	—	—	—	145.00
0.01588	0.99519	10.16	—	—
0.01822	—	—	—	135.00
0.03062	—	—	—	129.00
0.05062	—	—	—	121.00
0.06250	0.99745	17.22	—	—
0.07384	0.99758	—	0.820	114.82
0.09610	—	—	—	108.00
0.11222	0.99945	22.00	0.821	—
0.14062	—	—	—	98.00
0.17222	1.00150	26.18	0.833	—
0.25978	1.00447	28.91	0.847	—
0.37210	1.00654	35.34	0.860	—
0.46241	1.00767	39.26	0.867	—

TABLE 2—VALUES OF PARAMETERS A AND B OF ROOT'S EQUATION.

System	Temperature (°C)	A (g. l. mol^{-1} cm^{-3})	B (g. $l^{3/2}mol^{-3/2}$ cm^{-3})
Sodium formate in water	30	0.0436	0.0040
	35	0.0469	0.0071
	40	0.0496	0.0100
Sodium formate in 5% aqueous ethyl formate	30	0.0630	0.0329
	35	0.0420	0.0487

TABLE 3—VALUES OF ϕ_v^0 OF SODIUM FORMATE AT DIFFERENT TEMPERATURES IN WATER AND AQUEOUS ETHYL FORMATE.

System	Temperature (°C)	ϕ_v^0 (ml. mol^{-1})
Sodium formate in water	30	24.40
	35	21.30
	40	18.25
Sodium formate in 5% aqueous ethyl formate	30	5.00
	35	5.25

The greater magnitude of ϕ_v^0 in case of water suggests that the solute-solvent interaction is greater in case of water. Further, Table 3 shows that it decreases with increasing temperature in case of water and increases with temperature in case of aqueous ester.

Data on viscosity was analysed with the help of the Jones-Dole equation[17]:

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \quad \ldots \quad (4)$$

where η is the viscosity of the solution, η_0 is the viscosity of the solvent, C is the molar concentration and A and B are constants characteristic of the solute electrolyte. A coefficient represents the contribution from interionic electrostatic force[18]. The B coefficient is said to be a measure of the effective hydrodynamic volume of the solvated ions[19] and to denote the order or disorder introduced by the ions into the solvent structure. The values of A and B of equation (4) are determined from the intercept and slope of the straight line plots of $(\eta/\eta_0 - 1)/\sqrt{C}$ versus $\sqrt{C}$. These values for different solutions are given in Table 4.

TABLE 4—JONES-DOLE PARAMETERS AT DIFFERENT TEMPERATURES.

System	Temperature (°C)	A $mol^{-1/2}cm^{3/2}$	B $mol^{-1}cm^{3}$
Sodium formate in water	30	0.008	0.166
	35	0 01	0.181
	40	0.01	0.183
Sodium formate in 5% aqueous ethyl formate	30	−0.035	0.258
	55	−0.020	0.243

In the Jones-Dole equation, A is a calculable parameter and is similar for all 1:1 electrolytes. The A-parameter has been found to be 0.0093 ± 0.0009. The positive temperature coefficient of B-parameter, dB/dT, suggest that the salt behaves like a structure breaker[20] in case of water.

In case of solutions in aqueous ethyl formate the negative values of A has been obtained. However, the negative magnitude of A cannot be interpreted on the basis of Falkenhagen theory[21] and negative A values has been obtained in most of the cases involving mixed solvents[22,23]. The negative temperature coefficient of B, dB/dT suggest that the salts behave as a structure maker in the aqueous ester.

The limiting equivalent conductance of sodium formate in water and aqueous ethyl formate at different temperature is evaluated from Onsager's plots[24], and with the help of Owen method[25]. The limiting equivalent conductance, Λ_0, along with the Walden product, $\Lambda_0\eta_0$, is given in Table 5.

TABLE 5—LIMITING EQUIVALENT CONDUCTANCE, Λ_0, WALDEN PRODUCT, $\Lambda_0\eta_0$, FOR SODIUM FORMATE IN

Temperature (°C)	Λ_0 (Owen) ($ohm^{-1}cm^{2}$)	Λ_0 (Onsager) ($ohm^{-1}cm^{2}$)	$\Lambda_0\eta_0$
Water			
30	150.9	159.0	1.208
35	166.5	178.5	1.203
40	178.7	191.5	1.172
5% Aqueous Ethyl Formate			
30	138.7	139.0	1.269
35	156.9	156.0	1.272

The structural effects on the conductance of ions in solutions can be derived by a comparison of the Walden product (conductance-viscosity products) at different temperatures[20]. The negative temperature coefficient of the Walden product in water suggest that the salt behaves like a structure breaker in case of water and structure promotor in case of aqueous ethyl formate. These conclusions are in agreement with those derived from viscosity measurements.

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Study of Saponins from *Trigonella foenum-graecum* Linn. Leaves

I. P. VARSHNEY and D. C. JAIN

Department of Chemistry, G. S. Institute of Technology and Science, Indore 452 003

and

H. C. SRIVASTAVA and P. P. SINGH

Chemistry Division, Ahmedabad Textile Industry's Research Association, Ahmedabad 380 015

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The leaves of *Trigonella foenum-graecum* Linn. yields three saponin glycosides named as Graecunin A, Graecunin B and Graecunin C. Graecunin B has been identified as a glycoside of diosgenin with glucose, xylose and rhamnose as sugars in the molar ratio of (4 : 1 : 2).

TRIGONELLA foenum-graecum Linn. is a member of the family Leguminoseae, sub-family papilionaseae, commonly known as 'Maithi' in Hindi. The family Leguminoseae is known to be a rich source for the saponins and sapogenins both triterpenic and steroidal[1]. Leaves are used as vegetable throughout India.

A review of the literature shows that the seeds contain diosgenin[2-6,8], gitogenin[2,3-5,8], tigogenin[2,4-6,8], yuccagenin[6], yamogenin[8], neotigogenin[12]; the leaves contain diosgenin, gitogenin and tigogenin[7] and the stem contains diosgenin and an unidentified genin[7]. Inspite of all these works on sapogenin contents no work is reported on saponins and therefore this work was taken up. The present paper deals with the saponins from the leaves of this plant.

The green plants were purchased from the local market and the leaves and stems were separated and air dried. Powdered leaves were exhausted with petroleum ether and then with ethanol. The ethanol extract on concentration under reduced pressure gave a greenish brown syrupy mass, which was successively exhausted with petroleum ether, ether, carbon tetrachloride, chloroform, ethyl acetate and acetone in order to remove the substances soluble in these solvents. This gave a dark brown syrupy mass which was then dissolved in minimum quantity of methanol and precipitated in a large volume of ether/acetone. It gave a light brown powder, which gave all the tests for the steroidal saponins. On TlC it showed the presence of three major and a number of minor products and therefore it was chromatographed on silica gel column using chloroform : methanol : water (65 : 35 : 10) as eluant (40 fractions).

Fractions giving identical single spot on TLC were combined and the fractions giving mixtures were further separated by rechromatography using chloroform : methanol : water (20 : 12 : 3) as eluant and finally each product was rechromatographed on alumina column using petroleum ether, ethyl acetate, acetone and methanol as eluants which gave 3 pure saponins named as Graecunin A, B and C, respectively. The purity of the saponins was confirmed by TLC and electrophoresis.

Graecunin B had m.p. 154-56°, $[(\alpha)]_D - 46.8$ (C = 1%, MeOH) and R_f value (0.20) in chloroform : methanol : water (65 : 40 : 10). Graecunin B on acid hydrolysis with 2*N* sulphuric acid under reflux for 4 hours gave a genin which was separated and identified as diogenin by m.p., m.m.p., I.R. and TLC with authentic sample of diosgenin.

The hydrolysate was neutralized with freshly precipitated barium carbonate and deionised by ion exchange resin (Amberlite IRA 400 and IR 120 (H^+). The sugar solution on concentration and chromatography on Whatman filter paper No. 1 showed the presence of three sugars identified as glucose, xylose and rhamnose. The sugars were reduced with sodium borohydride to alditols, which were acetylated in the usual manner and yielded alditol acetates.

The alditol acetates were injected in the GLC apparatus where 3% ECNSS on chromosorb-W column was used and showed the presence of three sugars identified as glucose, xylose and rhamnose present in the molar ratio 4 : 1 : 2 (Fig 1). All the seven moles of the three sugars are therefore attached at C-3 OH group of diosgenin.

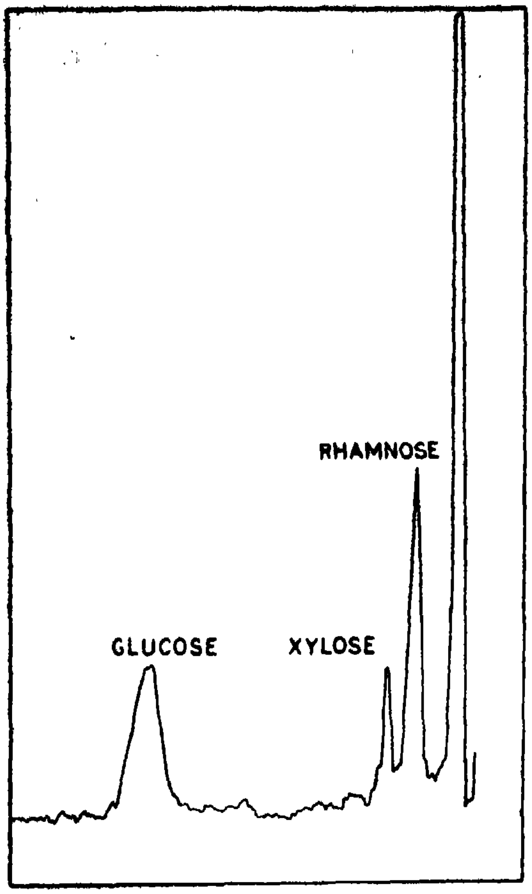


Fig. 1

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Thermodynamics of 1,10-Phenanthrolium Ion and its Iron(II) Complexes in Methanol-Water Mixtures at 298°K

G. BISWAS and S. ADITYA

Department of Applied Chemistry, University College of Science and Technology, 92, Acharya Prafulla Chandra Road, Calcutta-9 (India)

and

(Mrs.) A. BHATTACHARYYA and S.C. LAHIRI

Department of Chemistry, Kalyani University, Kalyani, Nadia (India)

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The equilibrium constants of the "isoelectric" reactions of the type

$$PhH^+ \rightleftharpoons Ph + H^+$$
$$FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+,$$
$$FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph,$$

have been determined *p*H-metrically and spectrophotometrically in methanol-water mixtures in 8-87 wt % in methanol. The enthalpies (consequently entropies) of ionizations have also been determined calorimetrically at 298°K. The inadequacies of electrostatic theories in explaining the thermodynamic parameters have been stressed. The importance of ionic solvation and structural contributions, though not well-understood, have been discussed.

THE analytical applications of 1,10-phenanthroline (Ph) and its iron-complexes, ferroin and ferrin are well-known. The dissociation constants of 1,10-phenanthrolium ion, ferroin and ferriin in aqueous solution have been determined by a large number of workers using different techniques[1].

The thermodynamic parameters of 1,10-phenanthroline were determined by Nasanen and Uusitalo[2] from temperature coefficient measurements of a cell without liquid-junction potential containing glass and Ag-AgCl electrodes. Lahiri and Aditya[3] determined the thermodynamic properties of 1,10-phenanthrolium ion and ferroin spectrophotometrically and that of ferriin using the data of George, Hanania and Irvine[4]. These values are in good agreement with the calorimetric values reported by Anderegg[5]. However, no systematic investigations have been made regarding the thermodynamic properties of the ligand and their complexes in solvents other than water. Such studies would be helpful in explaining the role of the solvents on the dissociation constants and other thermodynamic parameters and in gaining insight regarding the solute-solvent interactions.

Recently Lahiri, Biswas and Aditya[6] reported the thermodynamics of 1,10-phenanthrolium ion in ethanol-water solvents.

In order to elucidate the role of the solvents on the dissociation constants and the thermodynamic properties of the isoelectric reactions of the type,

$$PhH^+ \rightleftharpoons Ph + H^+ \quad (1)$$

$$FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+ \quad (2)$$

and

$$FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph \quad (3)$$

We studied the dissociation constants as well as enthalpies of the reactions (1), (2) and (3) in methanol-water mixtures *p*H-metrically, spectrophotometrically and calorimetrically. The results are reported in the present communication.

Experimental

The stock solution of the ligand was prepared by dissolving the weighed amount of 1,10-phenanthroline hydrate (E. Merck) in the desired solvents. Perchloric acid, caustic soda and acetic acid used were of analar grade. The solutions were prepared using double-distilled water from an all-glass apparatus. The preparation of ferrous-ammonium sulphate solution and purification of methanol have been described earlier[7].

The weight percentage of organic solvents in mixtures were determined in the same way as described before[8]. The dielectric constants of the solvent mixtures were calculated from the data by Bates and Robinson[9].

For the dissociation constants of the ligands in different percentages of mixed solvents, sodium acetate and acetic acid buffers as well as perchloric acid solutions were used.

The measurements were taken in solutions of very low ionic strengths $(10^{-3}-10^{-4} M)$ so that the dissociation constant values may be taken as the thermodynamic values.

The pK's of 1,10-phenanthrolium ion in methanol-water mixtures were determined spectrophotometrically in the manner described earlier.

The accuracy of the pK-values determined spectrophotometrically was further tested from pH-titration described earlier[6]. The average pK-values are given in table 1.

The concentrations of the complex were determined from O.D. readings and extinction coefficient values at these wavelengths. The average value of concentration of the complex was obtained from these measurements.

For the measurement of enthalpy of formation of 1,10-phenanthrolium ion in mixed solvents, excess of $HClO_4$ acid (concentration 0.2 N) was taken in the reaction Dewar. Spectrophotometric readings were taken with a Beckman D.U. spectrophotometer. The pH-readings were taken with Cambridge Bench type battery-operated pH-meter. The calorimeter used and the details of the enthalpy measurements have been described earlier[11,12].

TABLE 1—MEAN pK VALUES FOR 1,10-PHENANTHROLIUM ION AND FERROIN IN METHANOL-WATER MIXTURES AT 298°K

Wt. % of Methanol	pK_T for $PhH^+ \rightleftharpoons Ph + H^+$		Extinction coefficient values at		pK_a for reaction $FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+$ using calculated H^+ ion concentration	pK for $FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph$ using calculated H^+ ion concentration
	pH – meter	Spectrophotometer	500 nm.	510 nm.		
8	4.88	4.90	10745	11107	5.44	20.08
16.4	4.75	4.80	10907	11158	5.56	19.81
25.2	4.63	4.63	11152	11358	5.66	19.55
34.4	4.56	4.57	10914	11440	5.37	19.05
44.1	4.31	4.35	11026	11553	5.57	18.50
54.2	4.17	4.19	11356	11645	5.12	17.63
64.7	4.00	3.97	10577	10999	4.32	16.32
75.9	3.80	3.76	10611	10852	4.18	15.58
87.7	3.86	3.87	10708	11063	3.6	15.27

Ferrous-1,10-phenanthroline complex has an absorption maximum at 510 nm. The addition of methanol in the medium has no effect on the absorption band.

Under our experimental conditions, $FePh_3^{2+}$ was assumed to be the sole species[10] formed without any $FePh^{2+}$ and $FePh_2^{2+}$. The extinction coefficients of ferroin at 500 and 510 nm were determined from O. D. readings of solutions containing 10 to 20 fold excess of ligand to different amounts of ferrous ion where complete conversion of Fe^{2+} to $FePh_3^{2+}$ took place. The extinction coefficients of ferroin in different mixed solvents are given in columns 4 and 5 of table 1.

For the determination of stability constants of ferroin in mixed solvents, O. D's of solutions containing different amounts of Fe^{2+} ion (concn. range $5-25\times10^{-5}$ M) and phenanthroline (concn. range $5-25\times10^{-5} M$) were measured at 500 and 510 nm. The pH's ranged from 2.80 to 3.80.

Results

The thermodynamic dissociation constant K_T for the equilibrium $PhH^+ \rightleftharpoons Ph + H^+$ is given by

$$K_T = \frac{a_{Ph} \times a_{H^+}}{a_{PhH^+}} = \frac{C_{Ph} \times C_{H^+}}{C_{PhH^+}} \cdot \frac{f_{Ph} \times f_{H^+}}{f_{PhH^+}} \quad \dots \quad (4)$$

In our measurements, the hydrogen ion concentrations were of the order of $10^{-3}-10^{-4} M$ and the ionic strengths of the solutions were of the order of $10^{-3} M$ (even if acetate buffers were used), therefore, $\frac{f_{Ph} \times f_{H^+}}{f_{PhH^+}}$ can be approximated to unity.

Thus, $pK_T = pH + \log[C_{PhH^+}/C_{Ph}] - [B] + \log U_{H^+} + \log[C_{PhH^+}/C_{Ph}]$

$$= [B] + \log U_{H^+} + \log[(d_M - d)/(d - d_1)] \quad \dots \quad (5)$$

where [B] = meter reading in mixed solvents,

$\log U_H$ = correction factor in mixed solvent, and

d_M, d_i and d's are optical densities of the ligand in the molecular form, ionic form and at intermediate pH's. Knowing [B], $\log U_H$, d_M, d_i and d values at different percentages of the mixed solvents, pK_T values are determined.

For determination of pK by pH-metry, $\log [C_{PhH^+}/C_{Ph}]$ was determined from the fraction of neutralisation. Though the correction factors were known[12], yet we considered it desirable to calibrate the glass eletrode before each of the measurement in the way described before[13-15] to avoid any error creeping in the measurements due to changed asymmetry potential and sensitivity of the glass electrode.

Dissociation constants of ferroin complex

The equilibrium between ferroin and a strong acid may be represented as

$$FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+ \quad \dots \quad (12)$$

$$\text{Thus, } K_a = \frac{C_{Fe^{2+}} \times C_{PhH^+}}{C_{FePh_3^{2+}} \times C_{H^+}^3} \times \frac{f_{Fe^{2+}} \times f_{PhH^+}^3}{f_{FePh_3^{2+}} \times f_{H^+}^3}$$

$$= K_C \times f_{Fe^{2+}} \times f_{H^+}^3 / f_{FePh_3^{2+}} \times f_{H^+}^3 \quad \dots \quad (6)$$

Since, the measurements were made at very low ionic strengths, it is reasonable to assume $f_{Fe^{2+}} = f_{FePh_3^{2+}}$ and $f_{PhH^+} = f_{H^+}$, thus K_a becomes equal to K_c. The equilibrium constant values were evaluated using calculated values of H^+ ion concentrations.

The equilibrium constants K for the reaction, $FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph$,

$$\text{given by } K = \frac{[Fe^{2+}][Ph]^3}{[FePh_3^{2+}]} \quad \dots \quad (7)$$

is related to the equilibrium constants of reactions (1) and (2) in different solvents by the equation,

$$K = K_a \times K_T^3. \quad \dots \quad (8)$$

The values of the equilibrium constants are given in columns, 2,3, 6 and 7 of table 1.

The enthalpy values from the relation

$$\Delta H = \frac{-Q}{C} \quad \dots \quad (9)$$

where Q is the amount of heat evolved for the conversion of C grammoles of the Ph or Fe^{2+} into PhH^+ or $FePh_3^{2+}$ as under our experimental conditions all the ligands or Fe^{2+} will be converted into PhH^+ or $FePh_3^{2+}$.

The ΔH values for reactions (1) and (3) are given in table 2. The effect of ionic strengths on the isoelectric reactions (1) is small and so ΔH_1 can be taken as ΔH_1°.

The ΔH° values for reaction (2) can be calculated from ΔH° values for reactions (1) and (3). The thermodynamic properties ΔG°, ΔH° and ΔS° for the reactions (1), (2) and (3) are given in table 2.

TABLE 2—THERMODYNAMICS OF IONISATION OF PHENANTHROLIUM ION AND FERROIN IN METHANOL-WATER MIXTURES AT 298°K

Reaction	$PhH^+ \rightleftharpoons Ph + H^+$			$FePh_3^{2+} + 3H^+ \rightleftharpoons Fe^{2+} + 3PhH^+$			$FePh_3^{2+} \rightleftharpoons Fe^{2+} + 3Ph$		
Wt. % of MeOH	ΔG°/kJ mol^{-1}	ΔH°/kJ mol^{-1}	ΔS°/ $JK^{-1}mol^{-1}$	ΔG°/ kJ mol^{-1}	ΔH°/ kJ mol^{-1}	ΔS°/ $JK^{-1}mol^{-1}$	ΔG°/ kJ mol^{-1}	ΔH°/ kJ mol^{-1}	ΔS°/ $JK^{-1}mol^{-1}$
0	28.83[8]	17.03 (±0.20)	−39.8	30.46	80.63	168.2	116.90	131.04	47.3[8]
8.0	27.82 (±0.10)	18.37 (±0.20)	−31.8	31.05	87.77	190.3	114.56	142.88 (±1.0)	95.0
16.4	27.11	26.23	− 2.9	31.71	83.51	173.9	113.01	162.21	165.1
25.2	26.40	21.67	−15.9	32.30	105.60	246.0	111.55	170.62	198.3
34.4	26.02	19.04	−23.5	30.63	103.72	251.0	108.62	160.79	175.1
44.41	24.60	17.95	−22.2	31.76	99.29	226.5	105.56	153.18	159.8
54.2	23.76	18.37	−18.2	29.20	89.79	202.6	160.58	144.68	148.0
64.7	22.80	17.20 (±0.20)	−18.9	24.64	106.11	273.4	93.14	157.65 (±2.0)	216.5
75.9	21.67	—	—	23.85	—	—	88.87	—	—
87.6	22.01 (±0.40)	—	—	21.05	—	—	87.11	—	—

Discussion

The pK values of 1,10 phenanthrolium ion and ferroin in methanol-water mixtures are given in table 1. The pK-values of 1,10 phenanthrolium ion are found to be a linear function of (a) weight percent of methanol, (b) mole-fraction[16] of methanol and (c) $1/\epsilon$[17] where ϵ is the relative permitivity[17], upto 65% (wt) of methanol beyond which there are deviations. Only marginal improvement occurs if the activity of water is taken into consideration[18]. The pK-values in water may be had from the present measurement by extrapolation of any of these linear plots and these come out to be (a) 5.01, (b) 5.05 and (c) 5.03 in close agreement with our earlier value of 5.05 in water determined spectrophotometrically[8]. The results in columns 2 and 3 of table 1 show that the pK-values of 1,10 phenanthrolium ion passes through a minimum around 70 wt% of methanol similar to the observations by Paabo *et al*[19]. and Ohtaki[20]. For the reaction (3), a similar variation in pK values as in the reaction (1) is noted except for the minimum around 70 wt% of alcohol. For the reaction(2), the pK values increase first and then decrease.

The increasingly negative values of ΔG° for reactions (1) and (3) with increasing concentration of methanol indicate that the reactions are favoured in mixed solvents. For the reaction (2), the initial addition of alcohol up to 44 wt%, the reaction is not favourable, further increase in alcohol concentration favours the process. This is not unexpected since

$$\Delta G^\circ_{(2)} = \Delta G^\circ_{(3)} - 3\Delta G^\circ_{(1)}.$$

The analysis of the results in light of Born[21] equation, despite its limitations, shows that the dielectric constant is not the major factor affecting ionization, the main factor being solute-solvent interactions. The increase in the solubility of 1,10 phenanthroline in methanol-water mixtures and the difference in the solvational properties of PhH^+, H^+, Fe^{2+} and $FePh_3^{2+}$ are responsible for the variation in ΔG° values.

It has been said earlier that the structural modifications and ionic solvation have marked contribution to ΔH and ΔS but not on ΔG becuase of compensating

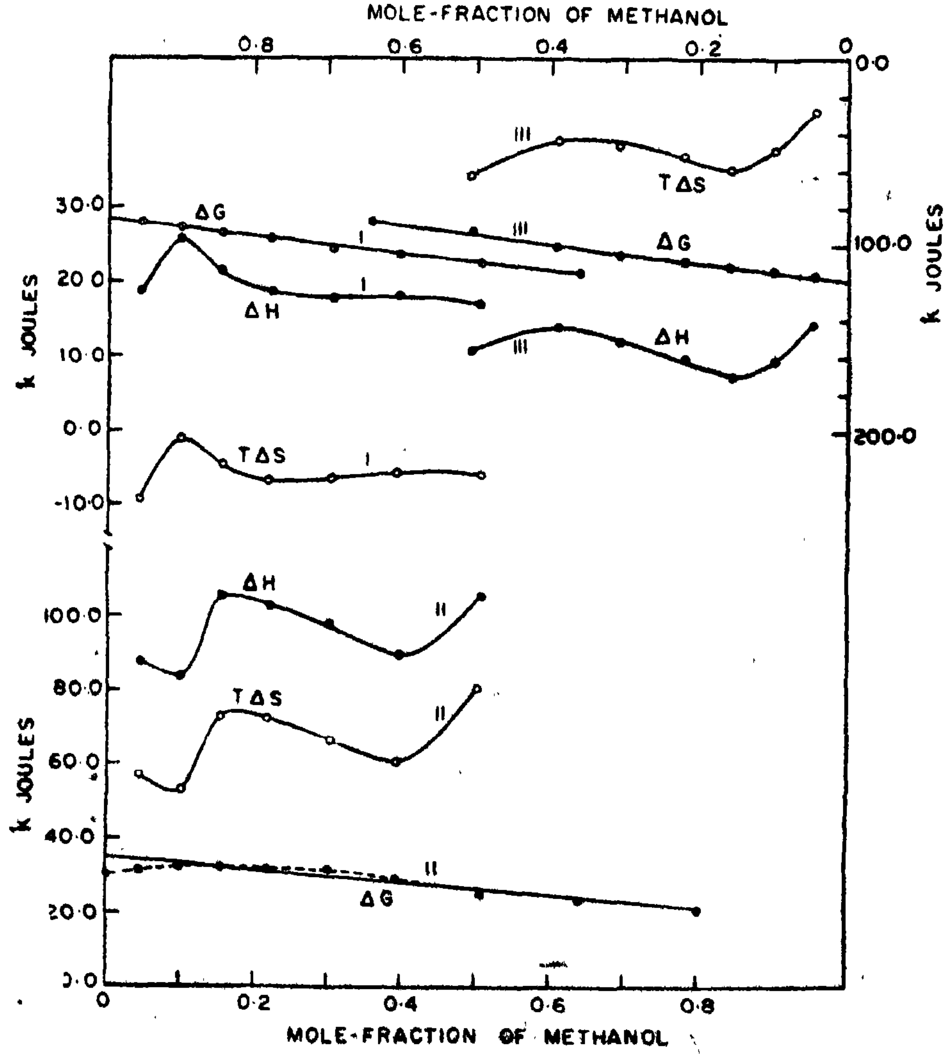


Fig. 1.

effects of ΔH and $T\Delta S$. Therefore the evaluation and interpretation of these parameters (ΔH and ΔS), though intriguing, seem worthwhile. The variations of ΔG°, ΔH° and $T\Delta S^\circ$ against mole fraction of methanol for the reactions (1), (2) and (3) are shown in the figure.

The values of ΔH for the reactions (1), (2) and (3) show appreciable variation with changes in solvent composition which is difficult to explain. Although there is lack of data in mixed solvents, wide variations of ΔH values have been reported for the ionization of water in DMSO-water mixtures[22,23] at 25° in methanol-water mixtures[24] and for the ionization of 4-substituted phenols in methanol-water mixtures[25]. The ΔH values by Avedikian[26] show an increase up to a mole fraction of 0.2 in alcohol in the case of ionization of acetic acid, but for benzoic acid ΔH shows a maximum around $x_2 = 0.3 - 0.4$, in methanol-water mixtures. These variations in ΔH with composition of solvent have been interpreted on the basis of variations in the structural properties of the solvent systems and ion-solvent interactions. Methanol-water system, it may be noted, shows a maximum in exothermic excess enthalpy of mixing at about $x_2 \approx 0.2$ (x_2=mole fraction of methanol), a minimum in $T\Delta S$ at $x_2 \approx 0.3$ and a maximum in the positive free energy change of mixing around $x_2 \approx 0.5$ [27].

Another process that needs mention is the preferential solvation of H^+ and Fe^{2+} compared to $FePh_3^{2+}$ and PhH^+ ions by water on the basis of electrostatic considerations, although the preferential solvation by the other solvent cannot be ruled out. Grunwald[28,29] and coworkers showed that certain cations like Na^+, K^+, H_3O^+ may be solvated by dioxane rather than hydrated in 50% dioxane-water mixtures. Nothing can however, be spelt out specifically about the solvation of ions in alcohol-water mixtures. The free-energy of transfer $\Delta G_t^\circ(H^+)$ of solvated proton from water to methanol-water mixtures up to 50% w/w of methanol, according to Wells[30] is equivalent to the transfer of a tetrahedral aquo-proton from water into the mixture and subsequent replacement of an H_2O molecule in the tetrahedron by a methanol molecule,

$$H^+(H_2O)_{4\,solv} + CH_3OH_{solv} \rightleftharpoons H^+(CH_3OH)(H_2O)_{3\,solv} + \text{water}$$

Such processes have profound effect on the enthalpy, and entropy changes of the reactions.

The breaking of $>N \rightarrow H^+$ and $>N \rightarrow Fe$ bonds results in the increase of ΔH° and ΔS° values. The structure-breaking process is endothermic accompanied with an increase in entropy while the structure forming process is exothermic associated with entropy-decrease[31-35]. Thus a number of interactions result in the variation of ΔH° and $T\Delta S^\circ$ of any reaction with composition of the solvent. ΔH° and $T\Delta S^\circ$ for the reaction (1) increase as the organic component increases and pass through maxima around $x_2 \approx 0.1$. The values of ΔH° and $T\Delta S^\circ$ for both reactions (2) and (3) show similar maxima around $x_2 \approx 0.15$. The ΔH° and $T\Delta S^\circ$ curves for reactions (1), (2) and (3), in general, show similar features. From the results one could infer that an overall increase in the structure of the solvent occurs which passes through a maximum around $x_2 \approx 0.15$. Similar observations have been made by Stern and Hansen[36] and Arnett[37] et al. This is also in agreement with the maxima reported for heats of solution of electrolytes in methanol-water around 20 mole per cent of methanol[38,39] and also with our earlier reports on 2,2′ dipyridyl and its iron(II) complexes[40] in ethanol.

Although the general nature of the ΔH° and $T\Delta S^\circ$ curves is the same, a comparison of the values of ΔH° and $T\Delta S^\circ$ for 2,2′ dipyridyl and its ferrous complexes with those of 1,10 phenanthroline and its complexes in methanol-water mixtures show considerable differences in the magnitude of the thermodynamic parameters. In case of dipyridinium and phenanthrolium and their tris complexes with iron(II) in water, the difference in ΔH was accounted for by Lahiri and Aditya[3] in terms of the difference in the resonance stabilisation energy of 1,10 phenanthroline and 2,2′-dipyridyl. In mixed solvents the difference is found to be changing with solvent composition. In addition to the difference in resonance stabilisation energy, the other factors that possibly come into play are (a) the hydrogen bonding capability of 1,10 phenanthroline and 2,2′ dipyridyl, (b) the fixed coplanarity of heterocyclic rings of phenanthroline compared to 2,2′ dipyridyl[41] and (c) the presence of dipyridyl predominantly as 'trans' form in water or in mixed solvents. The change in the enthalpy of protonation may be regarded as involving two equilibria, viz.,

(i) trans Dipy $\rightleftharpoons$ cis Dipy

(ii) cis Dipy + $H^+ \rightleftharpoons$ cis Dipy H^+

The first step is endothermic and the second an exothermic process[42]. For both the processes ΔH may be dependent on the composition of the medium.

With our present state of knowledge in the field, it is not possible to explain quantitatively the difference in the values of ΔH and $T\Delta S$ for 1,10 phenanthroline and 2,2′ dipyridyl and their iron(II) complexes methanol mixtures.

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Studies in Oxadiazoles. Part V : Synthesis of Some Amido (or Imido) Methyl Derivatives of 2-Amino/Mercapto-5-Aryl-1,3,4-Oxadiazoles as Potential Fungicides

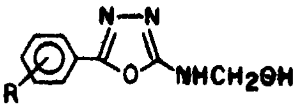
H. SINGH* and L. D. S. YADAV**

Chemistry Department, University of Gorakhpur, Gorakhpur, U.P.

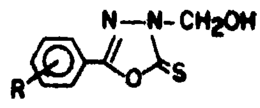
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Several 2-amido (or imido) methylamino-5-aryl-1,3,4-oxadiazoles (III) and 3-amido (or imido) methyl-5-aryl-1,3,4-oxadiazole-2-thiones (IV) have been prepared by condensing amide/imide with 2-hydroxymethylamino-1,3,4-oxdiazoles (I) and 3-hydroxymethyl-1,3,4-oxadiazole-2-thiones(II), respectively. Eighteen of these compounds have been compared with Dithane M-45, a commercial fungicide, in their fungitoxicity against *Aspergillus niger* and *Aspergillus flavus*, and most of these have exhibited fungicidal activity in the same range as Dithane M-45 at 1000 ppm.

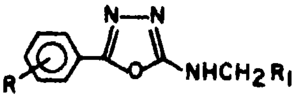
THE systemically active oxathiin fungicides require an aryl amide substituent for their enhanced activity[1] and the cyclic imide portion of several fungicides, like captan, folpet, difolatan and cycloheximide, has been suggested to be the toxic moiety[2-4]. The 2-amino/mercapto-1,3,4-oxadiazoles and their derivatives have been reported to possess pesticidal activities[5-11], and that no amido/imidomethyl oxadiazole of the type III or IV has apparently been reported so far. In view of above, it was presumed that the oxadiazole compounds (III and IV) with aryl amide/cyclic imide moieties might be fungicides of choice.



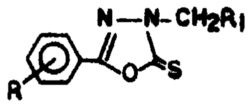
(I)



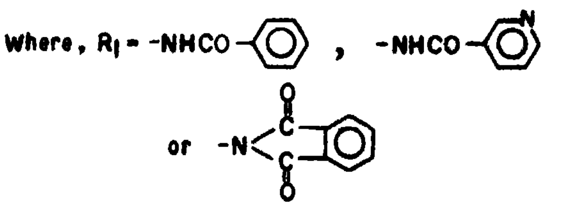
(II)



(III)



(IV)



2-Amino-5-aryl-1,3,4-oxadiazoles have been prepared according to the method of Gibson[11] by oxidative cyclisation of aldehyde semicarbazone with bromine and anhyd. sodium acetate. The 5-aryl-2-mercapto-1,3,4-oxadiazoles were prepared by the method of Young and Wood[12]. 2-Hydroxymethylamino-oxadiazoles (I)

TABLE 1—5-ARYL-2-HYDROXYMETHYLAMINO-1,3,4-OXADIAZOLES (I)

Sl. No.	R	Yield %	m. p. °C	Mol. formula	C(%) Found	C(%) Calcd	H(%) Found	H(%) Calcd
1	H	72	171	$C_9H_9N_3O_2$	56.32	56.54	4.89	4.71
2	*o*-Chloro	65	165	$C_9H_8N_3O_2Cl$	48.12	47.89	3.41	3.55
3	*p*-Chloro	70	190	$C_9H_8N_3O_2Cl$	47.96	47.89	3.62	3.55
4	*p*-Methoxy	68	186	$C_{10}H_{11}N_3O_3$	54.06	54.30	5.24	4.98
5	*p*-Nitro	61	179	$C_9H_8N_4O_4$	45.91	45.76	3.67	3.39

* For correspondence.

** Chemistry Department, M. G. Degree College, Gorakhpur, U.P.

were prepared[14] by the action of formaldehyde on 2-aminooxadiazoles, and similarly, 3-hydroxymethyl-oxadiazole-2-thiones (II) were obtained from the 2-mercapto-oxadiazoles. The condensation of compounds I with amide/imide in concd. H_4SO_4 gave III. On similar treatment II gave the compounds IV. The structures of the compounds were supported by IR data.

Experimental

5-Aryl-2-hydroxymethylamino-1,3,4-oxadiazoles (*I*) were prepared by heating appropria e 2-aminooxadiazole (0.1 *M*) and formaldehyde (0.1 *M*, 8.1 ml of 37% soln.) in DMF (20 ml) on water bath for 30-45 min. The reaction mixture was cooled, poured into water, filtered, the solid was washed with water for several

TABLE 2—5-ARYL-3-HYDROXYMETHYL-1,3,4-OXADIAZOLE-2-THIONES (II)

Sl. No.	R	Yield %	m. p. °C	Mol. formula	N(%) Found	N(%) Calcd.	S(%) Found	S(%) Calcd.
1	H	74	149	$C_9H_8N_2O_2S$	13.64	13.46	15.44	15.38
2	*o*-Chloro	61	139	$C_9H_7N_2O_2SCl$	11.41	11.55	12.97	13.20
3	*p*-Chloro	73	147	$C_9H_7N_2O_2SCl$	11.32	11.55	13.06	13.20
4	*m*-Methyl	59	170	$C_{10}H_{10}N_2O_2S$	12.91	12.61	14.15	14.41
5	*p*-Methyl	62	181	$C_{10}H_{10}N_2O_2S$	12.43	12.61	14.03	14.41

TABLE 3A—2-AMIDO (OR IMIDO) METHYLAMINO-5-ARYL-1,3,4-OXADIAZOLES (III)

Sl. No.	R	Yield %	m. p. °C	Mol. formula	C(%) Found	C(%) Calcd.	H(%) Found	H(%) Calcd.
				R_1 = *Benzamido*				
1	H	70	182	$C_{16}H_{14}N_4O_2$	65.04	65.31	4.63	4.76
2	*o*-Chloro	61	173	$C_{16}H_{13}N_4O_2Cl$	58.21	58.45	4.18	3.96
3[a]	*p*-Chloro	74	203	$C_{16}H_{13}N_4O_2Cl$	58.09	58.45	3.85	3.96
4	*p*-Methoxy	72	192	$C_{17}H_{16}N_4O_3$	63.21	62.96	5.06	4.94
5	*p*-Nitro	63	176	$C_{16}H_{13}N_5O_4$	56.49	56.64	3.64	3.83
				R_1 = *Nicotinamido*				
6[b]	H	65	187	$C_{14}H_{13}N_5O_2$	60.86	61.02	4.21	4.41
7	*o*-Chloro	56	162	$C_{15}H_{12}N_5O_2Cl$	54.41	54.63	3.60	3.64
8	*p*-Chloro	70	205	$C_{15}H_{12}N_5O_2Cl$	54.34	54.63	3.43	3.64
9	*p*-Methoxy	62	195	$C_{16}H_{15}N_5O_3$	60.13	59.08	4.74	4.62
10	*p*-Nitro	52	182	$C_{15}H_{12}N_6O_4$	52.63	52.94	3.61	3.53
				R_1 = *Phthalimido*				
11[c]	H	76	233	$C_{17}H_{12}N_4O_3$	63.96	63.75	3.86	3.75
12	*o*-Chloro	66	209	$C_{17}H_{11}N_4O_3Cl$	57.31	57.54	3.06	3.10
13	*p*-Chloro	79	241	$C_{17}H_{11}N_4O_3Cl$	57.86	57.54	3.31	3.10
14	*p*-Methoxy	72	201	$C_{18}H_{14}N_4O_4$	61.42	61.71	3.85	4.00
15	*p*-Nitro	61	196	$C_{17}H_{11}N_5O_5$	56.13	55.89	3.09	3.01

Significant bands (cm^{-1}) in IR spectra (in KBr)

	C=N,	C–O–C,	C=O,	Amino/amido, N–H	Substituted benzene/ pyridine nucleus
a.	1630	1027	1685	3348	1602, 1480, 860
b.	1626	1030	1653	3350	1587, 1493, 770, 685
c.	1637	1050	1733	3355	1605, 1464, 715

times and recrystallised from ethanol to give the desired product. The compounds thus prepared are recorded in Table 1.

5-Aryl-3-hydroxymethyl-1-3-4-oxadiazole-2-thiones (II)—The appropriate 2-mercaptooxadiazole (0.1 *M*) was dissolved in a minimum quantity of ethanol and formaldehyde (0.1 *M*, 8.1 ml of 37% soln.) was added. The mixture was refluxed for 1.5 hr, cooled, poured into water, filtered and the crude product was recrystallised from ethanol. The compounds thus prepared are recorded in Table 2.

2-Amido(or imido)methylamino-5-aryl-1,3,4-oxadiazoles (III)—The compound I (0.03 *M*) and amide/imide (0.03 *M*) were dissolved in a minimum quantity of concd. H_2SO_4 (75 ml) under cooling and stirred for 1 hr. The reaction mixture was poured on crushed ice, the residue filtered and recrystallised from ethanol. The compounds III thus prepared are recorded in Table 3A.

3-Amido (or imido) methyl-5-aryl-1,3,4-oxadiazole-2-thiones (IV) were prepared from compound II exactly in the same manner as the compound III from I. The compounds are recorded in Table 3B.

Fungicidal Screening The test organisms were *A. niger* and *A. flavus*. The antifungal activity was evaluated by agar-plate technique[14,15] at three concentrations *viz*. 1000 ppm, 100 ppm, and 10 ppm and the number of replications in each case was three. A commercial fungicide *Dithane M-45* was tested under

TABLE 3B—3-AMIDO (OR IMIDO) METHYL-5-ARYL-1,3,4-OXADIAZOLE-2-THIONES (IV)

Sl. No.	R	Yield %	m. p. °C	Mol. formula	N(%) Found	N(%) Calcd.	S(%) Found	S(%) Calcd.
				R_1 = *Benzamido*				
16[a]	H	71	170	$C_{16}H_{13}N_3O_2S$	13.41	13.50	10.06	10.29
17	*o*-Chloro	59	96	$C_{16}H_{12}N_3O_2SCl$	12.23	12.16	9.49	9.26
18	*p*-Chloro	65	104	$C_{16}H_{12}N_3O_2SCl$	12.01	12.16	9.53	9.26
19	*m*-Methyl	68	116	$C_{17}H_{15}N_3O_2S$	12.63	12.92	9.64	9.85
20	*p*-Methyl	70	140	$C_{17}H_{15}N_3O_2S$	12.74	12.92	9.71	9.85
				R_1 = *Nicotinamido*				
21	H	65	181	$C_{15}H_{12}N_4O_2S$	17.61	17.95	10.29	10.26
22	*o*-Chloro	64	106	$C_{15}H_{11}N_4O_2SCl$	16.36	16.16	9.43	9.24
23[b]	*p*-Chloro	68	132	$C_{15}H_{11}N_4O_2SCl$	16.50	16.16	9.01	9.24
24	*m*-Methyl	70	111	$C_{16}H_{14}N_4O_2S$	16.91	17.18	10.04	9.82
25	*p*-Methyl	72	121	$C_{16}H_{14}N_4O_2S$	17.34	17.18	9.56	9.82
				R_1 = *Phthalimido*				
26	H	71	162	$C_{17}H_{11}N_3O_3S$	12.11	12.46	9.56	9.50
27	*o*-Chloro	64	78	$C_{17}H_{10}N_3O_3SCl$	11.03	11.31	8.38	8.61
28[c]	*p*-Chloro	78	89	$C_{17}H_{10}N_3O_3SCl$	11.62	11.31	8.83	8.61
29	*m*-Methyl	66	108	$C_{18}H_{13}N_3O_3S$	13.31	13.33	9.84	10.16
30	*p*-Methyl	74	130	$C_{18}H_{13}N_3O_3S$	13.66	13.33	10.03	10.16

Significant bands (cm^{-1}) in IR spectra (in KBr)

	C=N,	C–O–C	C=O,	Amido, N–H	C=S,	Substituted benzene/pyridine nucleus		
a.	1625	1045	1660	3320	1332	1600,	1485,	680
b.	1613	1053	1667	3300	1330	1493,	837,	687
c.	1635	1040	1735	—	1320	1605,	1500,	860

TABLE 4—FUNGICIDAL SCREENING

Compound Serial as in Tables 3A & 3B	Average Percentage Inhibition after 96 Hours: Organism—*A. niger*, Concentrations used 1000 ppm	100 ppm	10 ppm	Organism—*A. flavus*, Concentrations used 1000 ppm	100 ppm	10 ppm
1	51.6	30.4	18.3	52.7	29.2	19.7
2	59.3	31.8	17.4	59.6	32.7	16.9
3	80.1	35.5	19.2	78.3	36.2	17.5
7	62.5	34.6	18.3	60.8	30.4	13.9
8	90.6	45.3	28.2	86.4	41.3	23.4
9	92.1	44.6	29.9	85.7	38.0	21.3
11	62.2	28.7	13.8	63.4	27.9	15.7
13	96.1	49.2	30.5	98.2	51.3	29.8
14	100	70.7	56.2	100	76.4	59.0
16	60.5	28.3	9.8	56.3	21.7	7.3
17	69.8	31.6	11.9	71.4	30.8	15.1
18	98.5	60.3	32.0	81.9	51.4	29.2
22	71.7	37.8	21.5	62.3	33.0	17.6
23	100	78.9	55.4	100	75.3	53.1
24	56.5	29.6	17.0	50.7	23.9	8.8
26	58.6	30.3	19.2	59.1	29.4	17.6
28	100	80.4	64.1	100	76.6	58.5
29	59.9	33.7	23.9	56.0	30.7	19.3
Dithane M-45 (A commercial fungicide)	100	86.0	71.2	95.3	80.6	65.9

similar conditions. The percentage inhibition by various compounds is recorded in Table 4.

$$\% \text{ Inhibition} = \frac{(C-T) \times 100}{C}$$

where, C = Diameter of fungus colony in control plates after 96 hours.

T = Diameter of fungus colony in treated plates after 96 hours.

Results and Discussion

The compound Nos. 3, 8, 9, 13, 14, 18, 23 and 28 exhibited the fungicidal activity almost in the same range as the commercial fungicide at 1000 ppm. The compound serial 14, 23 and 28 inhibited 100% the growth of both the fungal species at 1000 ppm, and appear to be more potent than the commercial fungicide against A. *flavus* at this concentration. It is noteworthy that in all such compounds chloro or methoxy group in aryl moiety appears to enhance the fungitoxicity considerably, and that the introduction of chloro group at *para* position is more effective as compared to *ortho* position.

The compounds IV were more active than the compounds III having similar substituents. This might be attributed to the presence of C=O and C=S groups in the compounds IV, as it has been observed earlier[16] that the combination of C=O and C=S groups sometimes works better than either alone. Further, the compounds IV contain -N-C=S linkage which is a possible toxophore in many pesticides[17,18].

The phthalimide compounds were more potent than their benzamido and nicotinamido analogues; this might be due to the presence of one additional C=O group[16] in the former. However, these results indicate that there is the following order of fungitoxicity in the

amido/imido derivatives :

phthalimido > nicotinamido > benzamido.

The most active compound serial 14, 23 and 28 inhibit > 50% the growth of both the test fungi even at 10 ppm, hence appear to be promising fungicides.

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Triethylamine Oxide and Iron(II) as Initiator of Methylmethacrylate Polymerization

AJIT K. BANTHIA*

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032.

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Triethylamine-oxide-Fe^{2+} redox system has been found to be an efficient initiator of aqueous polymerization of methylmethacrylate. Its mechanism has been found to be basically similar to the electron transfer mechanism of H_2O_2-Fe^{2+} or, N-haloamine-Fe^{2+} as initiator. This system incorporates only the amino end group (no hydroxyl) into the polymer to an extent of about one group per polymer molecule. A large portion of the total amino groups introduced into the polymer are quaternary in nature. This initiator system proves to be useful for the preparation of polymers containing amino groups at one end only.

THE demethylation reaction of N-amine oxide is known to proceed via free-radical intermediate[1,2]. The reaction may be caused by reducing metal salts e.g., Fe^{2+}, Cr^{2+}, V^{2+}, Ti^{2+} etc. in acidic medium.

The present study has been undertaken to examine the possibility of such systems as polymerization initiators in aqueous medium and to analyse the end groups of the resultant polymers by recently modified dye partition (extrapolation) method of Mandal and Palit[3,4] in order to elucidate the mechanism of the reaction.

Experimental

Methyl methacrylate (MMA), methyl acrylate, and acrylonitrile were purified by distillation under reduced pressure[5].

Triethylamine was treated with KOH beads and distilled. $FeSO_4.(NH_4)SO_4.6H_2O$ was used without further purification.

Aqueous polymerization of MMA was carried out at room temperature under nitrogen atmosphere in the dark. Triethylamine oxide was prepared as discussed in the literature[6,7]. A 22.5 ml. (0.20 mole) of 30% H_2O_2 was added with cooling to a solution of 0.10 mole of triethylamine and the resulting solution was allowed to stand overnight at room temperature with occasional warming. The method of Cope *et al*[8,9] for following the disappearance of amine and for decomposing the excess H_2O_2 has been followed. The required *p*H of the reaction mixture was achieved by adding sulfuric acid. The isolated polymers were washed with water and dried. The basic groups in the polymers were converted to salts by precipitating the benzene solution twice in acidified methanol[4]. Acid is omitted in the final precipitation step.

The number of average molecular weight ($\bar{M}_n$) of the polymer samples was determined osmometrically in tetrahydrofuran (THF) using a Hewlett-Packard 501 high speed membrane osmometer (08 membrane).

The dye partition (extrapolation) method of Mandal and Palit[3] was used for amino end group determination[3,4].

Results and Discussion

Triethylamine-oxide itself does not initiate polymerization in dark at room temperature, but act as a retarder for some vinyl polymerization[10]. However, in the presence of Fe^{2+}, it induces polymerization without any induction period. Table-1 summarizes the results of MMA polymerization obtained with triethylamine oxide-Fe^{2+} initiator system. The requirement of Fe^{2+} seems to be critical, concentration less than about $5x10^{-3}$ mol.l.$^{-1}$ does not constitute an efficient initiating system. A concentration as high as $1.5x10^{-2}$ mol.l.$^{-1}$ seems to effect a little lowering of the polymer yield. The concentration of triethylamine-oxide suitable for polymer preparation lies in the range 10^{-3}-10^{-2} mol.l.$^{-1}$. The number of average molecular weights ($\bar{M}_n$) of the polymers prepared with this initiator system are relatively low (ca. 10^4-10^5).

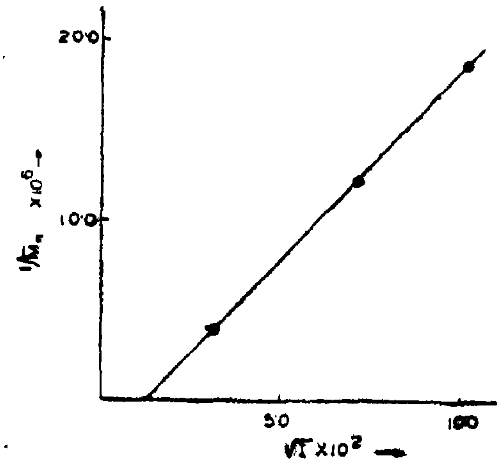
Free-radical nature of the polymerization is clearly evident from the fact that polymerization is inhibited in presence of conventional free radical scavengers viz., diphenylpicrylhydrazyl, hydroquinone, *p*-benzoquinone etc., and retarded effectively by atmospheric oxygen and the plot of $1/\bar{M}_n$ against the square-root of the initiator concentration (triethylamine-oxide) at a fixed concentration of Fe^{2+} and MMA is linear (Figure-1).

* Present Address: Laboratorium voor Organische Chemie, Rijksuniversiteit-Gent, Krijgslaan 272-S4, 9000 GENT, Belgium.

TABLE—1. RESULTS OF THE POLYMERIZATION OF METHYL METHACRYLATE (MMA) IN AN AQUEOUS SYSTEM.
INITIATOR : TRIETHYLAMINE-OXIDE + Fe^{2+}. [MMA] – 9.4×10^{-2} MOL. $l.^{-1}$; pH : 3.30 ;
N_2 ATMOSPHERE ; IN DARK AT ≃30°C.

Sample No.	$[(C_2H_5)_3NO]$ $\times 10$ mol. $l.^{-1}$	$[Fe^{++}] \times 10$ mol. $l.^{-1}$	Time of polymerization in hours	% yield	$\bar{M}_n \times 10^{-4}$	Number of Amino end groups per polymer molecule		
						Quaternary	Others	Total
1	1.02*	0.10	48	0	—	—	—	—
2	1.02*	1.00	48	0	—	—	—	—
3	1.02	10.00	3½	77.9	25.01	0.61	0.31	0.92
4	5.10*	1 00	48	0	—	—	—	—
5	5.10	5.00	3	53.6	10.23	0.70	0.35	1.05
6	5.10	10.00	3	76.1	8.18	0.65	0.33	0.98
7	5.10	20.00	1¾	69.2	9.23	0.76	0.36	1.12
8	10.20*	0.10	48	0	—	—	—	—
9	10.20*	1.00	48	0	—	—	—	—
10	10.20	5.00	1½	36.2	7.91	0.59	0.29	0.88
11	10.20	10.00	1½	68.0	5.35	0.66	0.34	1.00
12	10.20	15.00	1½	60.0	6.24	0.70	0.35	1.05

* No polymerization takes place.



Figure—1. Plot of reciprocal of number average molecular weight ($\bar{M}_n$) against square root of triethylamine oxide concentration (in mol. $l.^{-1}$).
$[Fe^{2+}] = 1 \times 10^{-2}$ mol. $l.^{-1}$ and
$[MMA] = 9.4 \times 10^{-2}$ mol. $l.^{-1}$.

The analysis of the polymers reveals that they possess only amino end groups to an extent of about one group per polymer molecule. A large fraction (≃66%) of the amino groups is quaternary in nature. These polymers contain no hydroxyl end groups as determined by dye-partition technique[3,11]. The failure to detect hydroxyl end groups in such polymers is probably due to the scavenging of hydroxyl ($\dot{O}H$) radicals by tertiary amine oxide or radicals derived from them[11]. From these results the following mechanism of primary radical generation is suggested :

$$Fe^{++} + (C_2H_5)_3N \rightarrow O + H^+ \begin{cases} \nearrow (C_2H_5)_3\dot{N}^+ + Fe^{3+} + OH^- & \text{(i)} \\ \searrow H_3C\text{-}\dot{C}H\text{-}N(C_2H_5)_2 + Fe^{3+} + H_2O & \text{(ii)} \end{cases}$$

Primary radicals produced in the reaction (i) incorporate a quaternary ammonium group in the polymers, whereas those produced in (ii) incorporate tertiary amine groups. It can be mentioned here that this mechanism is basically similar to the electron transfer mechanism of H_2O_2-Fe^{2+} and N-haloamine-Fe^{2+} as initiator of vinyl polymerization[4,12].

Ferris *et al*[1] suggested a similar reaction with trimethylamine oxide and Fe^{2+} in acidic medium.

$$(CH_3)_3\overset{+}{N}OH + Fe^{2+} + H^+ \rightarrow (CH_3)_3\dot{N}^+ + Fe^{3+} + H_2O \quad (iii)$$

Regarding the termination of poly (methyl methacrylate) (PMMA) radicals by ferric salts it has been established that PMMA radicals are not terminated by Fe^{3+} and/or $FeOH^{2+}$ in aqueous media[14-16]. Furthermore, incorporation of on average only one end group per polymer molecule rules out both the primary radical termination or, termination by mutual combination. Thus, it seems that here chain termination takes place predominantly through disproportionation of the growing polymer radicals. Incorporation of on average 1 end group per polymer molecule in case of aqueous polymerization of methyl methacrylate for various initiating systems was also realized by several workers[4,13,17,18] where it seems that chain termination of PMMA radicals takes place most predominantly through disproportionation. These results are in contrast to the claim that in aqueous heterophase polymerization, which mechanistically approaches emulsion polymerization, the termination of polymer radicals (here PMMA radicals), in the particle phase is effected predominantly by primary radicals and should incorporate on average 2 end group per polymer molecule[12]. Thus, it seems from this study that the accepted mechanism of termination by disproportionation for PMMA radical (based mostly on end group analysis of PMMA prepared in homogeneous non-aqueous media using dissociative initiator) is also true in case of aqueous heterophases polymerization of methyl methacrylate.

Although triethylamine oxide-Fe^{2+} is an initiator for MMA polymerization, no polymerization of acrylonitrile, methylacrylate and acrylamide occur with this initiator.

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Condensed Thiophene Derivatives. Part-II*. Formylation of Dibenzothiophene

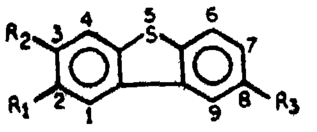
J. N. CHATTERJEA and R. S. GANDHI

Department of Chemistry, Patna University, Patna-800 005.

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Direct formylation of dibenzothiophene is reported.

No systematic attempts at formylation of dibenzothiophene have been reported. Hartough and Meisel[1] have proposed that various substituted carboxaldehydes may be synthesised from the corresponding acid chlorides by the Rosenmund reduction although none are so far reported. Dibenzothiophene was recovered in experiments on attempted formylation by conventional methods, *viz.* (a) N,N-dimethylformamide and phosphorus oxychloride[2], and (b) zinc cyanide and hydrogen chloride[3]. Riech and Co-workers[4] provided a useful method of formylation of aromatic heterocyclic compounds. Formylation of dibenzothiophene was carried out accordingly with dichloromethyl methyl ether in the presence of aluminium chloride at 0°. This afforded three different compounds identified as (I ; major, m.p. 125-26°), (III ; m.p. 236-37°) and (II ; as viscous liquid) in addition to unchanged dibenzothiophene. These carboxaldehydes (I, II, III) are characterised and identified by way of oxidation to related acids (IV, V, VI) and then subsequent preparation of methyl esters or alternatively by reduction of (I, II, & III) to corresponding methyldibenzothiophenes (VII, VIII, & IX).



I : R_1=CHO, R_2=R_3=H

II : R_2=CHO, R_1=R_3=H

III : R_1=R_3=CHO, R_2=H

IV : R_1=COOH, R_2=R_3=H

V : R_2=COOH, R_1=R_3=H

VI : R_1=R_3=COOH, R_2=H

VII : R_1=CH_3, R_2=R_3=H

VIII : R_2=CH_3, R_1=R_3=H

IX : R_1=R_3=CH_3, R_2=H

X : R_1=CH=CHCOOH, R_2=R_3=H

XI : R_2=CH=CHCOOH, R_1=R_3=H.

To illustrate, the major product melting at 125-26° was identified as dibenzothiophene-2-carboxaldehyde (I ; $\nu_{ald.\ carbonyl}$ 1705 cm^{-1}). (I) gave a *2,4-dinitrophenylhydrazone* and on oxidation by the method of Hey and Lobo[5] converted into (IV) which on subsequent esterification with diazomethane yields corresponding methyl dibenzothiophene-2-carboxylate. The authenticity of the structure (I) was further confirmed by reducing it by Wolff-Kishner method to give (VII). Similarly, the viscous liquid identified as dibenzothiophene-3-carboxaldehyde (II) ($\nu_{ald.\ carbonyl}$ 1708 cm^{-1}).

The product melting at 236-37° analysed for $C_{14}H_8O_2S$ and identified as dibenzothiophene-2,8-dicarboxaldehyde (i.r. absorption at 1700 cm^{-1}, split for dicarboxaldehydic group). The product (III) gave a *mono* 2,4-dinitrophenylhydrazone and a *di*aldoxime in alcohol. On reduction by Wolff-Kishner method (IX) was obtained. The authenticity of the structure (III) was confirmed by conversion into known 2,8-dimethyldibenzothiophene-5,5-dioxide. (IX) was characterised by the preparation of 2,4,7-trinitrofluorenone complex.

The carboxaldehydes (I) & (II) are converted into related cinnamic acids (X) & (XI) by Doebner's modification with malonic acid. Further work with these acids are in progress.

Experimental

**All m. ps. or b. ps. are uncorrected. Unless otherwise mentioned, the i. r. spectra were recorded in a Perkin Elmer Infrared Spetrophotometer, Model 237 in KBr discs.*

Formylation of Dibenzothiophene : A mixture of dibenzothiophene (4.0 g.) and anhydrous aluminium chloride (6.0g.) in dry methylene chloride (30.0 ml.) at 0° was stirred during dropwise addition of dichloromethyl methyl ether (6.0 ml. ; 70%) over a period of 15 min. ; when the evolution of hydrogen chloride ceased (15 min.), the reaction mixture was immediately poured on crushed ice which resulted into layers. The organic layer was separated out and the aqueous layer was extracted with chloroform and combined organic layers

* Part-I, is Chatterjea and Gandhi, This *Journal*, 1977, 54, 719.

were washed successively with water (2×30.0 ml.), sod. bicarbonate solution (2×30.0 ml. : 2N) and water (30.0 ml.). After drying over baked $MgSO_4$, the solvents were evaporated and the remainder taken up in benzene. The insoluble material was filtered out, the benzene solution was concentrated, cooled and chromatographed through an activated alumina column. It was eluted with benzene. Out of eight fractions, the first two fractions on evaporation of solvent gave unreacted dibenzothiophene, m.p. 99-100°.

Next three fractions gave an oil which was subjected to bulb distillation at a bath temp. 240-50°/2 mm. to give a light yellow oil. The oil on trituration and crystallisation from MeOH gave pale yellow prisms (0.8 g.), m.p. 125-26° and were identified to be *dibenzothiophene-2-carboxaldehyde* (I). (Found: C, 73.69 ; H, 3.87. $C_{13}H_8OS$ requires: C, 73.58. H, 3.80%); i.r. Spectrum: Carboxaldehydic absorption at 1705 cm^{-1}. The *2,4-dinitrophenylhydrazone* derivative was crystallised from a large volume of AcOH in orange crystalline solid, m.p. above 300°, (Found: N, 14.31 ; $C_{19}H_{12}N_4O_4S$ requires: N, 14.28%).

The remaining methanolic mother liquor from 3rd., 4th. & 5th. fractions was evaporated to give an oil which on distillation at a bath temp. of 220-30°/2 mm. gave a light yellow mobile liquid which was identified as *dibenzothiophene-3-carboxaldehyde* (II). (Found: C, 73.63 ; H, 3.86. $C_{13}H_8OS$ requires: C, 73.58 ; H, 3.80%). i.r. Spectrum: $\nu_{ald\cdot carbonyl}$ 1708 cm^{-1}. The *2,4-dinitrophenylhydrazone* derivative from dibenzothiophene-3-carboxaldehyde was crystallised from AcOH in an orange solid, m.p. 260-62°. (Found: N, 14.31. $C_{19}H_{12}N_4O$ requires: N, 14.28%). The rest three fractions on concentration and keeping at r.t. for 1 hr. gave a yellowish solid, which was crystallised from benzene in light yellow prisms (0.6 g.), m.p. 236-37°. It was characterised and identified as *dibenzothiophene-2, 8-dicarboxaldehyde* (III). (Found: C, 70.16 ; H, 3.72. $C_{14}H_8O_2S$ requires: C, 70.00 ; H, 3.36%). i.r. Spectrum: $\nu_{ald\cdot carbonyl}$ 1700 cm^{-1}. The *mono 2,4-dinitrophenylhydrazone* crystallised from a large volume of AcOH in an orange solid which melted above 300°. (Found: N, 13.43. $C_{20}H_{12}N_4O_5S$ requires: N, 13.53. $C_{26}H_{16}N_8O_8S$ requires: N, 18.66%). This clearly showed that only one carboxaldehydic group was involved in the formation of 2,4-dinitrophenylhydrazone derivative. *Dibenzothiophene-2,8-dialdoxime* crystallised from EtOH in colourless prisms, m.p. 246-48°. (Found: N, 10.41. $C_{14}H_{10}N_2O_2S$ requires: N, 10.37%).

Dibenzothiophene-2-carboxylic Acid (IV) : Dibenzothiophene-2-carboxaldehyde (0.64 g.) was converted into the corresponding 2-carboxylic acid by oxidising it with boiling silver nitrate solution (16.0 ml. ; 8%) for 3 min. Sod. hydroxide solution (5.0 ml. ; 15%) was added slowly till the free silver deposited on the inner walls of the flask completely disintegrated. The resulting alkaline mixture was boiled for 2 hrs., cooled, filtered and acidified to give the required *acid* (IV ; 0.35 g.) which was finally crystallised from AcOH, m. p. 251-52° (lit.[6], m.p. 253°). (Found: C, 68.35 ; H, 3.66. $C_{13}H_8O_2S$ requires: C, 68.42 ; H, 3.33%). *Methyl dibenzothiophene-2-carboxylate* prepared through diazomethane, melted at 80-81° (lit.[6], m.p. 74-75°). (Found: C, 69.35 ; H, 4.02. Calc. for $C_{14}H_{10}O_2S$: C, 69.42 ; H, 16%).

Dibenzothiophene-3-carboxylic Acid (V) similarly prepared and crystallised from EtOH in prismatic needles, m.p. 299-305° (decomp. ; lit[7], m.p. 300-305°). (Found: C, 68.51 ; H, 3.45. $C_{13}H_8O_2S$ requires: 68.42 ; H, .53%). *Methyl dibenzothiophene-3-carboxylate* crystallised from a mixture of MeOH & EtOH (1:1) to give colourless prismatic needles, m.p. 110-12° (lit.[7], m.p. 128-29°). (Found: C, 69.34 ; H, 3.56. Calc. for $C_{14}H_{10}O_2S$: C, 69.42 ; H, 4.16%).

2-Methyldibenzothiophene (VII) : The 2-carboxaldehyde isomer (0.5 g.) in dry diethylene glycol (5.0 ml.) was treated with hydrazine hydrate (1.0 ml. ; 99-100%) and boiled for 2 hrs. On cooling, the colourless *hydrazone* separated out. To this, pot. hydroxide (1.0 g.) was added after removing water from the system by distillation and heated to 190-200° for about 3 hrs. till evolution of nitrogen ceased. The mixture was cooled to r.t. and diluted with water and a crystalline mass separated out which was crystallised from EtOH as colourless plates (0.2 g.), m.p. 86-87° (lit.[8], m.p. 85.5°). (Found: C 78.67 ; H, 5.12. Calc. for $C_{13}H_{10}S$: C, 78.77 ; H, 5.09%). The *picrate* crystallised from EtOH in beautiful yellow needles, m.p. 115-16° (lit.[8], m.p. 117-18°). (Found: N, 9.92. Calc. for $C_{13}H_{10}S.C_6H_3N_3O_7$: N, 9.83%).

3-Methyldibenzothiophene (VIII) : similarly prepared and distilled under reduced pressure at 140-50°/2 mm. (Found: C, 78.81 ; H, 5.20, Calc. for $C_{13}H_{10}S$: C, 78.77 ; H, 5.09%). The *picrate* of 3-methyldibenzothiophene crystallised from EtOH in light yellow needles, m.p. 95-96° (lit.[8], m.p. 97°). (Found: N, 9.96. Calc. for $C_{13}H_{10}S.C_6H_3N_3O_7$: N, 9.83%).

2,8-Dimethyldibenzothiophene (IX) crystallised from pet. ether in colourless short needles, m.p. 154-55° (lit.[9], m.p. 121-2?°). (Found: C, 79.15 ; H, 5.87. $C_{14}H_{12}S$ requires: C, 79.25 ; H, 5.66%). It is quite possible that our product is probably purer than that reported by Armarego and Turner or it may be a polymorphic form. The *2,4,7-trinitroflurenone* complex crystallised from benzene in orange needles, m.p. 210-11°. (Found : N, 8.20. $C_{14}H_{12}S.C_{13}H_5N_3O_7$ requires N, 8.12%).

2,8-Dimethyldibenzothiophene-5,5-dioxide : To a cold solution of glacial AcOH (3.0 ml.) and hydrogen peroxide (2.0 ml. ; 20 vol.) was added 2,8-dimethyldibenzothiophene (0.1 g.) and refluxed for 2 hrs. The reaction mixture was diluted with cold water to give a yellowish precipitate which was filtered and crystallised from dilute AcOH in colourless needles (0.05 g.), m.p. 294-295° (lit.[9] m.p. 297-98°). (Found: C, 68.91 ; H, 5.04. Calc. for $C_{14}H_{12}O_2S$: C, 68.84 ; H, 4.95%).

Dibenzothiophene-2(B)-acrylic acid (X) : Catalytic amount of piperidine was added to a mixture of dibenzothiophene-2-carboxaldehyde (0.21 g.) and malonic acid (0.11 g.) in dry pyridine (5.0 ml.) and was heated on water-bath for 5-6 hrs. It was cooled, diluted with water and the *acrylic acid* (X) was obtained on acidification with dilute hydrochloric (5N). It was crystallised from EtOH in prisms (0.2 g.), m.p. 251°. (Found: C, 70.92 ; H, 4.01. $C_{15}H_{10}O_2S$ requires: C, 70.86 ; H, 3.96%).

Dibenzothiophene-3(B)-acrylic Acid (XI) similarly prepared, crystallised from EtOH in colourless prisms, m.p. 238-39°. (Found: C, 70.88 ; H, 4.12. $C_{15}H_{10}O_2S$ requires: C, 70.86 ; H, 3.96%).

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Studies on the Use of Acetothioacetanilide as a Gravimetric Reagent for Zinc, Cadmium and Mercury

TARASANKAR PAL and JOYTIRMOY DAS

Department of Chemistry, The University of Burdwan, Burdwan 713104, West Bengal (India).

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Zinc (8-33 mg), cadmium (10-30 mg) and mercury(II) (18-54 mg) have been determined by weighing their *bis*-complexes with acetothioacetanilide of general formula $M(C_{10}H_{10}ONS)_2$, M standing for Zn, Cd or Hg. The ranges of complete precipitation are 7.0-7.5, 6.9-8.7 and 1.3-1.8 respectively. Separation of Cd^{2+} from Zn^{2+} is possible in the presence of citrate, from Pb^{2+} in the presence of triethanolamine and from Mg^{2+}, UO_2^{2+}, Cr^{3+} and Al^{3+} in the presence of tartrate. Mercury(II) can be separated from Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, MoO_2^{2+}, Sb^{3+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Th^{4+}, Zr^{4+}, VO^{2+}, VO^{-1}, MoO_4^{2-} and TeO_4^{2-} when sufficient Na_2-EDTA is added. Tartrate can also be used to mask Fe^{3+}, while Pb^{2+}, Mn^{2+}, Mg^{2+} and Al^{3+} do not interfere at the *p*H of precipitation of mercury(II). Cadmium and mercury(II) have also been separated by controlling the *p*H. Only AsO_3^{3-} has been found not to interfere with the determination of zinc. However, the zinc content of several samples of non-ferrous alloys have been determined after separating the foreign ions using an anion exchanger, Dowex-50-WX8 (Cl^-). The relative standard deviations are ±0.5%, ±0.31% and ±0.14% respectively for zinc, cadmium and mercury(II).

ZINC(II), cadmium(II) and mercury(II) prefer polarisable ligands due to their 'softness'. However, mercury(II) has the greatest cation deformability among these ions. Thus it is not surprising to find more organic ligands forming thermally stable chelates with mercury(II) in comparison to zinc(II) or cadmium(II).

Although quinoxaline-2-carboxylic acid and its derivatives[1] have been recommended for the gravimetric determination of zinc, they are of limited use due to poor selectivity. The thiourea-Reinecke's salt method[2,3] is still used widely for the determination of cadmium as the other organic precipitants recommended, viz. 2-(*o*-hydroxyphenyl)-benzoxazole[4], 1-phenyl-tetrazoline-5-thione[5] and 1-immino-3-thioisoindoline[6] have low selectivity. Only N-phenylbenzohydroxamic acid[7] appears to have good selectivity in acetate medium. Mercury(II) on the other hand has been determined using precipitants containing nitrogen and sulphur[8-14] as well as oxygen[15-20].

Acetothioacetanilide, $CH_3COCH_2CSNHC_6H_5$ having coordination sites at one oxygen and one sulphur atoms has been used in this investigation for the direct gravimetric determination of zinc(II), cadmium(II) and mercury(II). All the complexes have metal to ligand ratio 1 : 2 and the relative stabilities are in the order of Hg>Cd≈Zn. Thus, mercury(II) has been separated from a number of diverse ions by masking them, while the scope of using such sequestering agents decreases in case of cadmium or zinc. Zinc has been determined in several samples of brass and other alloys.

Experimental

Acetothioacetanilide solution: The reagent was prepared following the method of Barnikow, Kunzek and Richter[21]. A 1.4% solution of the reagent in 50-60% ethanol was prepared.

Standard zinc solution: A stock solution was prepared by dissolving metallic zinc (G.R., E.Merck) in dilute hydrochloric acid. The metal content was estimated by titration with Na_2-EDTA[22].

Standard cadmium solution: Hydrated-cadmium sulphate (G.R., E.Merck) was dissolved in dilute sulphuric acid and the cadmium content was determined by the thiourea Reinecke's salt method[2,3].

Standard mercury(II) solution: Mercuric chloride (G.R., E.Merck) was dissolved in dilute nitric acid and the metal content was determined gravimetrically with benzoyl-*m*-nitroacetanilide[10].

Diverse ions: Stock solutions were prepared from pure samples of nitrates, chlorides and sulphates of various metal ions.

Apparatus: A Cambridge *p*H Meter and a photo-recording Metriplex Derivatograph OD-102 (Hungary) were used.

Procedure for zinc: Dilute a known quantity of zinc solution containing 8-33 mg of zinc to 150 ml and add 1 g of sodium chloride. Raise the *p*H to above 6.0 with dilute ammonia (1*M*) and warm slightly

(30-35°). Add the reagent (0.30-0.35 g) solution with stirring and adjust the *p*H between 7.0-7.5 with aqueous ammonia (1*M*). Digest the complex formed on a hot (40°) water-bath for about 30 min. Filter the white precipitate, wash with water at room temperature and dry at about 90-95°. Calculate the zinc content using a factor of 0.1453.

Procedure for cadmium: Dilute the solution containing 10-30 mg of cadmium to 150 ml, adjust the *p*H to 5.0-6.0 with aqueous ammonia (2*M*) and heat to 70-80° after adding 1-2 g of sodium chloride. Add 13-15 ml of the reagent (0.18-0.21 g) solution with stirring. Raise the *p*H to 7.5-8.0 with aqueous triethanolamine (20%) or ammonia (1*M*). Allow the lemon-yellow voluminous precipitate to cool down (~20°) by placing in a water-bath. Filter through a sintered glass crucible of fine porosity, wash the cold water and dry at 100°. Use 0.2262 as the factor for determining the cadmium content.

When cadmium was precipitated in the presence of foreign ions, the appropriate masking agent was added before the reagent.

Procedure for mercury(II): Dilute an aliquot of the mercury solution containing 18-54 mg of the metal to 150 ml and adjust the *p*H to 1.3-1.8 using dilute nitric acid. Add 5-10 ml of the reagent (0.07-0.14 g) solution with stirring. Leave the mixture on a hot water-bath for about 20 min and stir occasionally. Filter, wash with hot (70-80°) water and dry at 120°. The conversion factor is 0.3429.

In order to effect separation of mercury(II) from foreign ions Na_2-EDTA was added before adding the reagent.

The results of the determination of all the three metals are given in Table 1.

TABLE 1—DETERMINATION OF ZINC, CADMIUM AND MERCURY

Metal taken (mg)	Wt. of ppt. (mg)	Metal found (mg)	Rel. error (%)
Zn^{2+} 32.7	225.4, 225.1	32.8 , 32.7	0.03, nil
Zn^{2+} 16.4	112.6, 112.5	16.4 , 16.4	nil , nil
Zn^{2+} 8.2	56.3, 56.3	8.2 , 8.2	nil , nil
Cd^{2+} 34.0	150.0, 150.0	33.93, 34.0	−0.20, nil
Cd^{2+} 28.3	124.9, 124.8	28.2 , 28.2	+0.35, +0.35
Cd^{2+} 22.6	100.4, 100.2	22.7 , 22.7	+0.44, +0.44
Hg^{2+} 54.5	156.4, 156.6	53.6 , 53.7	−0.18, −0.36
Hg^{2+} 36.3	106.0, 106.1	36.3 , 36.3	nil , nil
Hg^{2+} 18.2	52.5, 53.0	18.0 , 18.1	−1.09, −0.54

Results

The nature of the complexes: The colour of the complexes changed from very pale yellow to yellow in the order zinc, cadmium and mercury. The solubility in ethanol (95%) increased in the reverse order though it was very low in dilute alcohol in all the cases.

Mercury(II)-*bis*-acetothioacetanilide complex when precipitated from solutions at 30° was yellow in colour and was moderately soluble in ethanol, though the solubility was low in acetone, chloroform or isobutyl methyl ketone. The complex was yellow when dried at 90–95° but turned greenish above 100°. On boiling the freshly precipitated complex for some time it turned black slowly.

TABLE 2 DETERMINATION OF CADMIUM IN PRESENCE OF DIVERSE IONS, Cd (II) TAKEN=28.3 mg.

Diverse ion (mg)	Condition	Wt. of complex (mg)	Cd^{2+} found (mg)	Rel. error (%)
Zn^{2+} , 100	a	125.9, 125.5	28.5, 28.4	+0.70, +0.35
Pb^{2+} , 100	b	125.8, 126.0	28.4, 28.5	+0.35, +0.70
Mg^{2+} , 100	c	126.0, 125.2	28.5, 28.3	+0.70, nil
Hg^{2+} , 100	d	124.9, 125.0	28.2, 28.3	−0.35, nil
UO_2^{2+}, 100	c	124.8, 126.0	28.2, 28.5	−0.35, +0.70
Cr^{3+} , 100	c	124.8, 125.1	28.2, 28.3	−0.35, nil
Al^{3+} , 100	c	125.1, 125.2	28.3, 28.3	nil , nil
In^{3+} , 100	c	125.6, 125.4	28.4, 28.4	+0.35, +0.35

(a) Citrate added (b) Triethanol amine added
(c) Tartrate added (d) *p*H separation.

TABLE 3—DETERMINATION OF MERCURY (II) IN PRESENCE OF DIVERSE IONS, Hg (II) TAKEN=36.3 mg.

Diverse ion (mg)	Masking agent	Wt. of complex (mg)	Hg (II) found (mg)	Rel. error (%)
Zn^{2+} , 100	a	105.9, 106.0	36.3, 36.3	nil , nil
Cd^{2+} , 100	a	106.1, 106.1	36.4, 36.4	+0.27, +0.27
Cu^{2+} , 100	a	106.1, 106.0	36.4, 36.3	+0.27, nil
Pb^{2+} , 100	—	106.0, 106.0	36.3, 36.3	nil , nil
Ni^{2+} , 100	a	106.0, 106.1	36.3, 36.4	nil , +0.27
Co^{2+} , 100	a	106.1, 105.9	36.4, 36.3	+0.27, nil
Mn^{2+} , 100	—	105.9, 105.8	36.3, 36.2	nil , −0.27
Mg^{2+} , 100	—	106.0, 106.0	36.3, 36.3	nil , nil
Be^{2+} , 100	—	106.1, 106.0	36.4, 36.3	+0.27, nil
VO^{2+} , 100	—	106.1, 106.1	36.4, 36.4	+0.27, +0.27
VO_2^{2+} , 100	a	106.0, 106.1	36.3, 36.4	nil , +0.27
MoO_2^{2-}, 100	a	105.8, 105.9	36.2, 36.3	−0.27, nil
Sb^{3+} , 100	a	105.9, 105.9	36.3, 36.3	nil , nil
Bi^{3+} , 100	a	106.0, 106.1	36.3, 36.4	nil , +0.27
Fe^{3+} , 100	a	106.1, 105.9	36.4, 36.3	+0.27, nil
Fe^{2+} , 100	b	105.9, 105.8	36.3, 36.2	nil , −0.27
Al^{3+} , 100	—	106.0, 105.8	36.3, 36.2	nil , −0.27
Cr^{3+} , 100	a	106.0, 106.0	36.3, 36.3	nil , nil
Ti^{4+} , 100	a	106.0, 106.0	36.3, 36.3	nil , nil
Zr^{4+} , 100	a	105.8, 106.0	36.2, 36.3	−0.27, nil
Ce^{4+} , 100	a	106.0, 105.8	36.3, 36.2	nil , −0.27
VO_3^- , 100	a	106.1, 105.9	36.4, 36.3	+0.27, nil
MoO_4^{2-}, 100	a	106.1, 105.9	36.4, 36.3	+0.27, nil
TeO_4^{2-} , 100	a	106.0, 106.0	36.3, 36.3	nil , nil

(a) Na_2-EDTA, (b) Na-K tartrate.

Samples of pure complexes were analysed for nitrogen by Kjeldahl's (micro) method and for sulphur by conversion to sulphate. The metal contents were also determined in case of zinc and cadmium after decomposing the ligand. The experimental

Reqd. for $M(C_{10}H_{10}ONS)_2$,%	Found,%
Zn, 14.53 ; N, 6.23 ; S, 14.23	Zn, 14.44 ; N, 6.11 ; S, 14.11
Cd, 22.62 ; N, 5.64 ; S, 12.90	Cd, 22.52 ; N, 5.71 ; S, 13.19
Hg, 34.29 ; N, 4.78 ; S, 10.93	Hg, — N, 4.68 ; S, 10.95

results indicated that *bis*-complexes were formed.

Thermogravimetric studies: Appropriate weights of the complexes were mixed with aluminium oxide and subjected to heating at the rate of 12° per min. The thermogravimetric curves showed that the thermal stability of the complexes are in the order Zn$<$Cd$<$Hg, the decomposition commenced at 95-100°, 110° and 135° respectively. The decomposition of the zinc complex became vigorous from 280° and finally a loss of 81.5% (calculated loss for conversion of ZnR_2 to ZnO, 81.7%) was recorded. Similarly, the rapid decomposition of the cadmium complex commenced at 215° and finally, a loss of 73.5% was recorded while the conversion of CdR_2 to CdO required 74.1%.

Effect of the concentration of the reagent: Approximately 100% and 75% excess of the theoretical quantity of the reagent was required for the quantitative precipitation of zinc and cadmium respectively at *p*H 7.0. But the mercury complex was completely precipitated at *p*H 1.8 when only a marginal excess of acetothioacetanilide was added. When more of the reagent was added the mercury(II) complex changed colour from yellow to greenish yellow though the weight remained unchanged.

Effect of pH: Zinc started precipitating at *p*H 5.2 and cadmium at 5.9 and the ranges for quantitative precipitation were 7.0-7.5 and 6.9-8.7 respectively. At higher *p*H the effect of hydrolysis was prominent. In case of mercury, the range of complete precipitation was *p*H 1.3-1.8. At lower *p*H there was a tendency of decomposition of the complex producing sulphide.

Effect of sequestering agents: Excepting borate and fluoride almost all common masking agents interfered in the determination of zinc. Cadmium was masked by cyanide, phosphate and disodium-EDTA, though the presence of citrate; tartrate, triethanolamine, salicylate, borate, fluoride and iodide showed no adverse effect. The precipitation of mercury was not marked by disodium-EDTA, tartrate or iodide.

Effect of diverse ions: The presence of AsO_3^{3-} did not interfere with the determination of zinc.

The quantitative precipitation of cadmium was possible from Al^{3+}, In^{3+}, Mg^{2+}, VO^{2+} and Cr^{3+} using 1 g of sodium potassium tartrate as the masking agent, while 1 g of citric acid was used when zinc was present. Triethanolamine masked lead. Mercury(II) may be precipitated at *p*H 1.5 and cadmium can be determined in the filtrate by the same reagent by raising the *p*H.

Several ions, e.g. Pb^{2+}, Mn^{2+} and Mg^{2+} did not interfere with the determination of Mercury(II) at *p*H 1.8, while Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Bi^{3+}, Fe^{3+}, Al^{3+}, Cr^{3+}, UO_2^{2+}, Th^{4+}, Zr^{4+}, MoO_2^{2+}, Sb^{3+}, Cu^{2+}, Ce^{4+}, VO^{2+}, VO_3^-, MoO_4^{2-} and TeO_4^{2-} had to be masked by sufficient Na_2-EDTA.

Determination of zinc in alloys: Several non-ferrous alloys were dissolved in hydrochloric acid and hydrogen peroxide and zinc was separated on an anion-exchanger. The process due to Gerdes and Rieman[23] was modified for the alloys concerned.

The mixture of the metal ions obtained by dissolving the alloys was passed through a column of 20-50 mesh Dowex 50-W-X8 (Cl^-) of 11 cm in height and 1.3 cm internal diameter. The column was washed with water and all other metal ions present (Ni^{2+}, Cu^{2+}, Fe^{3+}, Pb^{2+}, Al^{3+}) were eluted with 50 ml of 0.5*M* hydrochloric acid. Zinc was subsequently eluted with 100 ml of 0.5*M* nitric acid and determined gravimetrically with acetothioacetanilide. A flow rate of 7 ml/min was maintained all through.

The experimental results are given in Table 4.

TABLE 4—DETERMINATION OF ZINC IN ALLOYS

Composition of the alloy (%)	Alloy taken (mg)	Zn found (mg)	Rel. error (%)
Zn 77.00	27.6	77.0	nil
Cu 22.92		77.1	+0.13
Zn 40.40			
Cu 56.50	43.67	40.32	−0.19
Pb 2.56		40.30	−0.24
Fe 0.10			
Zn 29.83			
Cu 61.24, Sn 1.48		29.81	−0.06
Ni 2.15, Fe 1.50	51.52	29.89	+0.20
Pb 1.02, Al 1.38			
Mn 1.30, P 0.05			

Precision and accuracy; The relative standard deviations were ±0.5%, ±0.31 and ±0.14% for zinc, cadmium and mercury(II) respectively. The confidence limits (95%) for the same are Zn, 16.36 ± 0.62; Cd, 24.39±0.22 and Hg, 36.34±0.10.

Discussion

The mercury(II)-*bis*-acetothioacetanilide complex varied in colour from yellow to yellow-green depending on the temperature of drying though the weight remained unchanged: The thermal analysis curves with several samples were also identical.

When sodium or potassium chloride was added to enhance coagulation, the cadmium complex decomposed at ~100°, but this temperature was ~65° when ammonium chloride was added though apparently the same complex was formed. The procedure for zinc will be of limited application but those for cadmium and mercury(II) are more accurate and selective than many existing methods.

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Studies on the Kinetics of the Oxidation of Leucine with Metaperiodic Acid

(Miss) SUSHILA and K. C. GROVER

Department of Chemistry, University of Jodhpur, Jodhpur (India)

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The oxidation of leucine by metaperiodic acid has been studied. The rate was found to be directly proportional to the concentrations of leucine as well as metaperiodic acid. The effect of temperature showed that the Arrhenius equation is valid in this case. The values of the energy of activation, entropy of activation and free energy of activation have been found to be 24.8 K. cals./mole, 2.6 e.s.u. and 23.9 K. cals/mole respectively.

Studies on the effect of pH showed that the rate constant increases with increasing pH. The probable reactive species are $H_3IO_6^{--}$ and leucine ions. A suitable mechanism has been proposed for the reaction.

SOME work seems to have been done on the kinetics of the oxidation of leucine by different oxidants[1-3], but no work has been done on its kinetic studies with metaperiodic acid which has been attempted here.

Experimental

Reagents used: The reagents used were As_2O_3 (0.002*M*), periodate ($2.5\times10M^{-2}$) and leucine ($2.5\times10^{-2}M$). The chemicals used were B.D.H. Anala-R. products and were used without any further purification.

Procedure: To 25 ml. 0.02*N* periodate solution (except in case of use of excess of periodate) was added the requisite quantity of buffer. After keeping it for half an hour in the constant temperature bath, an equivalent quantity (25ml., 0.02N) of leucine (which had been kept at the same temperature of the bath for about half an hour) was added (except in cases of use of excess of leucine) and the volume made upto 100 ml. The timer was started during the mixing. Samples(10 ml.) were removed at known intervals of time and quenched in 25 ml. of 0.002*M* arsenite solution (0.0033*M* in case of use of excess of periodate to which 5 ml. of saturated solution of sodium bicarbonate and 1ml. of 5% KI solution has been added). The excess arsenite was titrated with 0.002*M* iodine solution (0.0033*M*. in case of use of excess periodate) after keeping it for 20 minutes, using starch as indicator.

Reaction Rates: The following tables indicate the nature of the results obtained. Graphs were plotted for all results and the specific rate constants k_1 (first order) and k_2 (second order) obtained from the slope of graphs for log (a-x) and (I/a-x) against time in seconds.

Dependence of Rate on Reductant Concentration: The effect of various concentrations of leucine on the rate was studied in the range $6.25\times10^{-3}M$ to $25.00\times10^{-3}M$ and the results showed that the rate is proportional to the concentration of leucine.

Dependence of Rate on Oxidant Concentration: The effect of variation of metaperiodate concentration have been studied in the range $3.57\times10^{-3}M$ to $6.25\times10^{-3}M$ periodate concentration. The results showed that the rate is proportioned to the periodate concentration.

TABLE 1—EFFECT OF ADDITION OF DIFFERENT ELECTROLYTES

Temperature = 40±0.05° pH ~ 8.5
Leucine = $1.25\times10^{-3}M$ Iodine = 0.002*M*
Periodate = $2.5\times10^{-3}M$ Added salt = $25\times10^{-3}M$

Salt added	Nil	CH_3COONa	NaCl	$NaNo_3$	Na_2SO_4	CH_3COOK	KCl	KNO_3	K_2SO_4
$K_2\times10^{-3}$ litre mole.$^{-1}$ sec.$^{-1}$	3.68	1.90	2.37	3.52	5.40	2.72	2.51	4.13	6.10

TABLE 2—EFFECT OF TEMPERATURE

Leucine = $1.25\times10^{-3}M$ | pH 8.6
Periodate = $2.5\times10^{-3}\ M$ | Iodine = $0.002M$

Temperature °C	30	35	40	45
$K\times10^{-3}$ Litre mole^{-1}sec.$^{-1}$	1.21	2.33	3.68	8.50

Results and Discussions

Order of the Reaction: The reaction between leucine and metaperiodate has been shown to be of second order. The values of first order rate constants show that the rate is directly proportional to their concentrations, the overall order being two.

Influence of Addition of Different Electrolytes on Reaction Rate: The results (table-1) show that the presence of acetate and chloride ions retards the rate while sulphate ion increases it. Nitrate ions had no effect on the rate while potassium ion slightly increased the same.

pH Effect: The rate was found to increase with increasing pH. The second order rate constants at $40\pm0.05°$ were plotted against the pH and calculated values of $(H_3IO_6^{--})\times(C_6H_{12}NO_2^-)$ (Fig. 1). The two curves were found to coincide with each other showing thereby that probable reactive species is $(H_3IO_6^{--})$ and $(C_6H_{12}NO_2^-)$ ions.

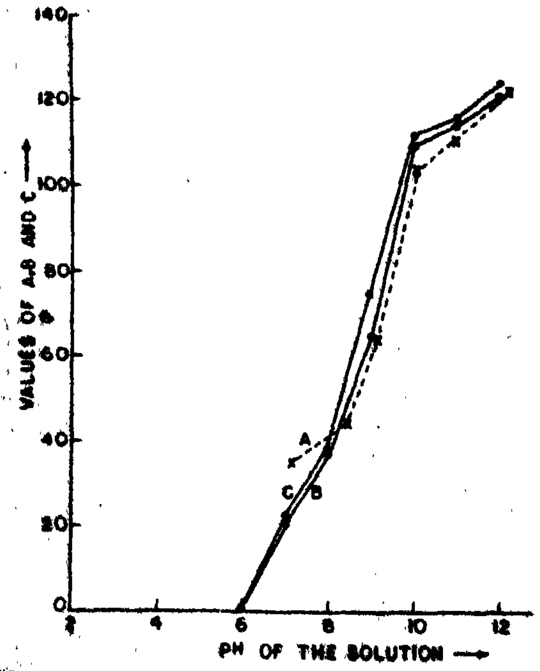


Fig. . Leucine vs Periodate

A—×...× Experimental values of $K_2\times1.2\times10^3$ at 40°C.

B—○—○ Calculated values of $[H_3IO_6^{--}]\times[C_6H_{12}NO_2^-]\times10^8$ at 25°C.

C—●—● Calculated values of $[H_3IO_6^{--}]\times[C_6H_{12}NO_2^-]\times10^7$ at 25°C.

Mechanism: On the basis of the results obtained in table-(table 1), a graph was plotted between 1/K and 1/Red. when a straight line was obtained which did not pass through the origin showing that complex formation takes place in this case. Mercuric chloride test[3] for free radical was found to be negative.

The end products were identified as isovaleric acid, ammonia and carbon dioxide. The formation of isovaleric acid was further confirmed by the formation of its derivatives amide (m.p. 139°) and benzylamide (m.p. 56°). The effect of pH on reaction rate (Fig. 1) showed that the probable reaction species may be $(H_3IO_6^{--})\times(C_6H_{12}NO_2^-)$. The probable mechanism of the reaction can be represented as follows where step V seems to be the rate determining step.

$$(CH_3)_2CH\ CH_2CH\ NH_2\ COOH \xrightarrow[I]{Fast} [(CH_3)_2CH\ CH_2\ CH\ NH_2\ COO^-]+H^+$$

$$2H_4IO_6^- \xrightarrow[II]{Fast} 2\ H_3IO_6^{--}+2H^+$$

$$[(CH_3)_2CH\ CH_2CH\ NH_2COO^-]+H_3IO_6^{--} \xrightarrow[III]{Fast} [(CH_3)_2CH\ CH_2\langle^{NH_2}_{COO}\rangle H_3IO_6^{--}]$$

$$[(CH_3)_2CHCH_2CH\langle^{NH_2}_{COO}\rangle H_3IO_6^{--}] \xrightarrow[Fast]{IV} (CH_3)_2CH\ CH_2CHO+NH_3+IO_3^-+2OH^-+CO_2$$

$$(CH_3)_2CHCH_2CHO+H_3IO_6^{--} \xrightarrow[Slow]{V} (CH_3)_2CH\ CH_2\ COOH+IO_3^-+OH^-+H_2O$$

Isovaleric acid.

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Voltammetric Studies of Fe(II) and Fe(III)-N-[Tris (hydroxy-methyl) methyl] glycine Complexes

J. K. JAILWAL*, JAI KISHAN and R. C. KAPOOR

Department of Chemistry, University of Jodhpur, Jodhpur-342 001 (India)

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The complex formation of N-(tris(hydroxymethyl) methyl glycine (Tricine) with ferrous and ferric ions has been studied voltammetrically at a rotating platinum electrode at different *p*H values. With ferrous ions 1:1 and 1:2 complex species were found to form with stability constants of 3.51×10^7 and 1.68×10^6 respectively. In the case of ferric ion only 1:1 complex with stability constant of 6.16×10^9 could be evaluated under the experimental conditions, although an indication for the formation of a second 1:2 complex species was obtained.

N-[TRIS(hydroxymethyl) methyl] glycine (tricine), first synthesised by Good[1], has proved quite useful as a buffer in the *p*H range of physiological interest[2,3]. By E.M.F. measurements, Bates *et al.*[4] have reported some standard thermodynamic parameters of ampholyte tricine in 50% methanol.

Tricine has a tendency to form complexes with many metal ions in which hydroxymethyl groups of the ligand can also participate in complexation. Complexometric studies of tricine with Co(II), Ni(II), Cu(II) and Zn(II) have been conducted by Visles *et al.*[5] using conductivity and potentiometric techniques. Some IR and magnetic susceptibility measurements of the solid chelates were also reported. In the authors' laboratory[6], complex formation of tricine with some metal ions like Cd(II), Pb(II), Cu(II) and Zn(II) has been investigated polarographically. These metal ions were found to form 1 : 1 and 1 : 2 chelates and at higher *p*H values in the alkaline range they have a tendency to form hydroxy complexes. The polarographic behaviour of Eu(III) and In(III) in tricine has also been investigated.

Systems which undergo electrochemical reactions in the anodic potential range (>0.2V vs SCE) can be studied satisfactorily with the platinum electrode. The authors have used rotating platinum electrode (RPE) quite successfully in the studies of Fe(III, II)-glycine[7], Tl(III)-glycine, Tl(III)-α-alanine and Tl(III)-N,N-dihydroxy ethylglycine complexes[8]. In the present paper voltammetric study of complexes of tricine with Fe(II) and Fe(III) is being reported, wherein RPE has been employed as the indicator electrode.

Experimental

An automatic polarograph-Radelkis type OH 102, was used for recording current-voltage curves at a scanning rate of 250 mV/minute. The working electrode consisted of a platinum wire 11.0 mm in length and 0.75 mm in diameter which was fused at the lower end of a glass tube in the direction parallel to the axis of the tube. A Sargent synchronous motor was used to rotate the electrode at a speed of 600 rpm. Electrode connections were made by filling the electrode tube with mercury. The potential values are given against a saturated calomel electrode (SCE). Before recording any voltammogram, the electrode was cleaned by treating it with hot nitric acid for nearly 10 minutes and then washed thoroughly with distilled water.

The studies were carried out at different *p*H values in 1*M* KCl as supporting electrolyte. Pure nitrogen gas was used for the deaeration of the experimental solutions which were kept at a constant temperature of $30 \pm 0.1°$. All reagents used were of analytically pure grade. Tricine supplied by Sigma Chemical Company (USA) was used as such in the above studies.

Results

The half-wave potential values of the waves obtained for the oxidation of Fe(II) and the reduction of Fe(III) in the presence of different concentrations of tricine are given in Table 1.

The influence of change in *p*H value on the waves for the oxidation of Fe(II) and the reduction of Fe(III) in 50-folds excess of tricine is shown in figures 1 and 2 respectively. In case of oxidation of Fe(II), the slope of the log-plot of the wave increased with increase in *p*H upto *p*H 5 and thereafter the wave started breaking up into two. At *p*H 6.5, a great decrease in wave height was observed. The wave tended to disappear above *p*H 7. The values of log-plot analyses are given in Table 2. For the reduction of Fe(III), a tendency for the second wave to appear can be noted even at a *p*H value of 3.5.

* Present Address : Quality Control Laboratories, Indian Drugs and Pharmaceuticals Limited, Hyderabad-500037, India.

TABLE 1—VARIATION IN $E_{\frac{1}{2}}$ VALUES FOR Fe (II) AND Fe (III)-TRICINE SYSTEM

Fe(II) CONCN. $5\times10^{-4}M$, Fe(III) CONCN. $5\times10^{-4}M$.

Concentration of Tricine (M)	$E_{\frac{1}{2}}$/V vs SCE for Fe (II)-Tricine System at pH 3	Fe (II)-Tricine System at pH 5	Fe (III)-Tricine System at pH 3	Fe (III)-Tricine System at pH 9
0	+0.500	—	+0.410	—
1.25×10^{-2}	+0.495	+0.430	+0.370	—
2.50×10^{-2}	+0.480	+0.380	+0.340	−0.530
5.00×10^{-2}	+0.457	+0.332	+0.312	—
1.00×10^{-1}	+0.435	+0.285	+0.285	—
1.50×10^{-1}	—	+0.242	—	—
2.00×10^{-1}	+0.415	+0.190	+0.257	−0.535
3.00×10^{-1}	—	+0.160	—	—
4.00×10^{-1}	+0.390	+0.145	+0.230	−0.540
5.00×10^{-1}	—	+0.130	—	−0.540
6.00×10^{-1}	+0.380	—	+0.210	—

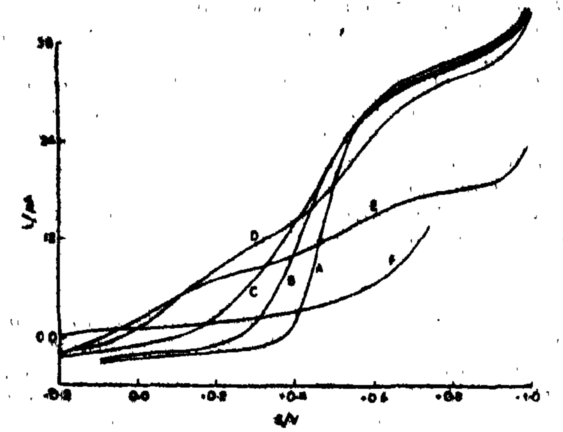


Fig. 1. : Effect of pH on the oxidation waves of Fe-(II)-tricine system ; pH 3(A), 4(B), 5(C), 6(D), 6.5(E) and 8(F).

Fe(II) concn. $5\times10^{-4}M$; Tricine concn. $2.5\times10^{-2}M$

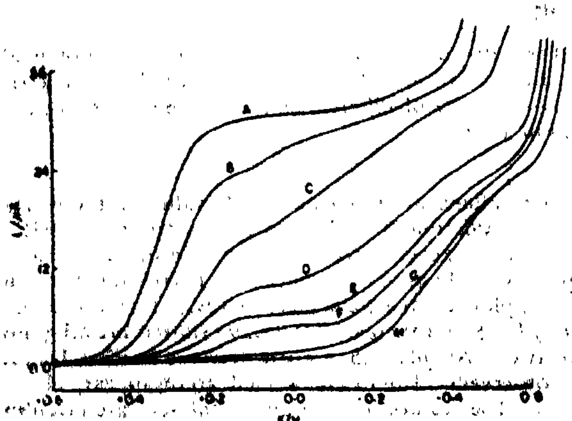


Fig. 2. : Effect of pH on the reduction waves of Fe(III)-tricine system ; pH 3(A), 3.5(B), 4(C), 4.5(D), 5(E), 6(F), 7(G) and 8(H).

Fe(III) concn. $5\times10^{-4}M$; Tricine concn. $2.5\times10^{-2}M$.

TABLE 2—LOG-PLOT ANALYSIS VALUES FOR Fe(II)-TRICINE SYSTEM

Fe (II) CONCN. 5×10^{-4} M ; TRICINE CONCN. 2.5×10^{-2} M.

pH	Slope	$E_{\frac{1}{2}}$V vs SCE
2.5	0.080	+0.500
3.0	0.081	+0.480
3.5	0.110	+0.450
4.0	0.125	+0.420
4.5	0.145	+0.405
5.0	0.177	+0.380

Discussion

The Fe(II)-Fe(III) system exhibited irreversible character at the RPE in 1M KCl. For a reversible electrode reaction involving one-electron change, the slope of log-plot analysis of the wave should be nearly 0.06V. In the present case, the value of the slope for the oxidation of Fe(II) was obtained as 0.08V whereas for the reduction of Fe(III) it was found to be 0.09V, suggesting the irreversible nature of the redox system. There is a difference of about 0.09V in the $E_{\frac{1}{2}}$ values of the oxidation and reduction waves of iron, which also supports the above conclusion.

The Fe(II)-Fe(III) system is known to be diffusion controlled at RPE[8]. For an irreversible diffusion controlled electrode process, the change of the half-wave potential of the metal ion with ligand concentration(X) can be expressed in a simplified way as

$$E_{\frac{1}{2}c}=E_{\frac{1}{2}s}+\frac{0.06}{\alpha n}\log K_{diss}-p\frac{0.06}{\alpha n}\log[X] \quad (1)$$

at 30°C. At 1M concentration of the complexing agent this simplifies to

$$E_{\frac{1}{2}c}=E_{\frac{1}{2}s}+\frac{0.06}{\alpha n}\log K_{diss} \quad (2)$$

which can be used quite conveniently for evaluating the stability constant of the complex. The notations used have their usual significance. Here α is the transfer coefficient of the electrode process, given by

$$E=E_{\frac{1}{2}}+\frac{0.06}{\alpha n}\log\frac{i_d-i}{i} \quad (3)$$

According to expression (1), for a complex species in solution, a plot between $E_{\frac{1}{2}c}$ and log [X] should give a straight line with a slope equal to $-p\frac{0.06}{\alpha n}$. Thus, the

number of ligand (molecules (p) attached to the metal ion can be calculated. If more than one metal-complex species are formed then in that case correspondingly more than one straight lines can be obtained and each one may be treated in the same way.

The effect of different tricine concentration on the oxidation of Fe(II) has been studied at pH 3 and 5. The influence is evident in the plot of $E_{\frac{1}{2}c}$ vs log [tricine] as given in figure 3.

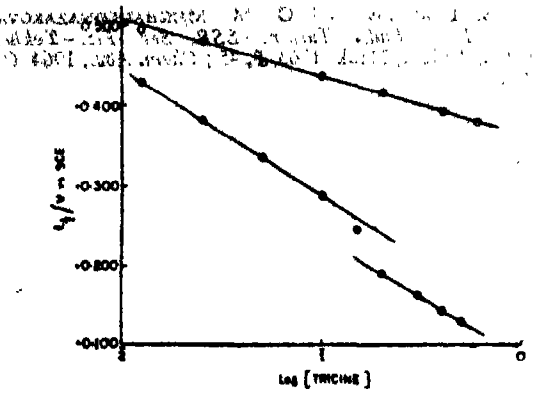


Fig. 3. : Plot of $E_{\frac{1}{2}}$ vs. log [tricine] for Fe(II)-tricine system at pH 3(○) and 5(●).

At pH 3, this plot gave a straight line, indicating the formation of one complex species. The slope of this line was found to be 0.075V and the value of α was obtained as 0.75, which gave the value of p as $0.94 \simeq 1$. Thus at this pH value the formation of 1 : 1 complex is indicated.

Two separate straight lines of almost same slopes were obtained at pH 5. The first line was obtained for tricine concentration of 0.0125 to 0.100M whereas the second one was found in the concentration region of 0.200 to 0.500 M tricine. The values of the slope and α corresponding to the first straight line were 0.160V and 0.34 respectively, giving the value of p as $0.903 \approx 1$. In the case of the second curve, the α was obtained as 0.75 which is equal to that for the oxidation of simple Fe(II). The slope of the plot was 0.155V which gave the value of p as $1.94 \simeq 2$. Thus at pH 5, in addition to 1 : 1, a second 1 : 2 complex between Fe(II) and tricine is also formed.

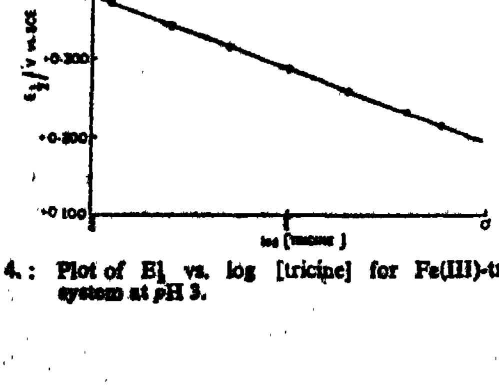


Fig. 4. : Plot of $E_{\frac{1}{2}}$ vs. log [tricine] for Fe(III)-tricine system at pH 3.

Similarly, for Fe(III) system at pH 3, a straight line with a slope of 0.095V was obtained (figure 4), which gave the value of p as $1.05 \simeq 1$ by using the value of α as 0.67.

For the evaluation of stability constants, the value of $E_{\frac{1}{2}c}$ at ligand concentration of 1M i.e., log[X]=0 can be found out from the plot of $E_{\frac{1}{2}c}$ vs log[X]. This value together with the values of α, $E_{\frac{1}{2}s}$ and n can be used in expression (2) to calculate stability constant. At the experimental pH values of 3 and 5, the value of stability constant so calculated will correspond to the apparent stability constant since at these pH values tricine does not dissociate completely. The real stability constants were obtained by multiplying the apparent stability constants by $\Sigma \frac{HX}{X^-}$ (HX=tricine) at the experimental pH values. At pH 3 and 5, the values of this quantity were obtained as 1.269×10^{5} and 1.00×10^{3}, using pK_1 and pK_2 values of tricine as 2.40 and 8.00 respectively. The real stability constants of different complexes are given in Table 3.

TABLE 3—STABILITY CONSTANT VALUES

System	pH	α	p	Stability Constant
Fe (II)-Tricine	3	0.75	1	3.51×10^{7}
	5	0.34	1	—
	5	0.75	2	1.68×10^{9}
Fe (III)-Tricine	3	0.67	1	6.16×10^{6}

For Fe(III)-tricine system, the reduction wave started breaking up into two even at a pH value of 3.5 in 50-folds excess of tricine (0.025M). At pH values greater than 3, the wave pattern itself was found to vary with tricine concentration, even at a constant pH value. At pH values in alkaline range, again a single (although not well defined) wave was obtained. In this region, the half-wave potential value of the wave remained almost independent of the ligand concentration, as is evident from the values at pH 9 (Table 1).

Therefore, the system was studied only at pH 3 at which the formation of 1 : 1 complex species was confirmed. The system could not be studied at pH values higher than 3, for obvious reasons. The breaking up of the reduction wave into two can indicate, as in the case of Fe(II), the formation of two complex species viz. 1:1 and 1:2, although it was not possible to evaluate the second complex species of Fe(III)-tricine system under the experimental conditions.

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Gravimetric Determination of Selenium using N-Benzene-sulphonylhydroxylamine as Reducing Agent

L. R. MALEWAR and K. SATYANARAYANA

Department of Chemistry, College of Science, Raipur, 492 002 (M.P.)

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The method described here allows determination of selenium by reduction of selenious acid in hydrochloric acid using N-benzenesulphonylhydroxylamine. The procedure is particularly useful when selenium has to be determined in presence of tellurium. The method is rapid and simpler than the longer and time-consuming conventional methods and gives results which compare in precision. Analysis of synthetic samples containing selenium and tellurium using the separation method gave acceptable results except in the case of metals which form insoluble chlorides. The proposed procedure is accurate and relatively free form interferences.

A series of hydroxamic acids have been applied for the determination of metal ions. N-Benzoylhydroxylamine has been shown to be a useful reagent for the spectrophotometric and gravimetric determination of several metals[1]. There is, however, little quantitative information on the N-benzenesulphonylhydroxylamine as an analytical reagent. Unlike the benzohydroxamic acid, the proposed reagent showed negative tests for iron, copper, but precipitates elementary selenium quantitatively in presence of hydrochloric acid.

The literature on selenium determination contains a number of methods based on the reduction of selenium(IV) and (VI) to elemental selenium. The metal is generally determined as its red variety with reducing agents such as sulphur dioxide[2], hydroxylamine hydrochloride[3], thiourea[4] and copper(I) chloride[5]. N-Benzenesulphonylhydroxylamine is a very convenient reagent for the gravimetric determination of selenium. The method described here allows rapid determination of selenium in the range of 9.21 to 207.36 mg. It has been applied to the analysis of selenium–tellurium mixtures with a relative standard deviation of less than 0.2%. The reaction can be carried out in the presence of EDTA and tartaric acid which may be used for masking the interfering metals such as copper, bismuth, arsenic and antimony.

Experimental

Selenium solution : In preparing selenium solution, (10mg of Se/ml) an approximate amount of the reagent grade selenious acid (BDH) was dissolved in water and diluted to a litre. The amount of selenium was gravimetrically determined by the hydroxylamine hydrochloride[3].

Preparation and properties of the reagent : N-Benzene-sulphonylhydroxylamine was prepared by the action of benzenesulphonylchloride on hydroxylamine following the literature procedure[7]. The reagent is a colourless crystalline compound and is freely soluble in water, alcohol and acetone, m.p. 126°. For use as precipitant, the solution of the reagent, 4 percent (w/v) is generally employed. Hydrochloric acid (BDH. A. R. sp.gr.1.16) was employed for regulation of acidity. For evaluating the extent of interferences, solutions were prepared from reagent grade chemicals to contain known amounts of the ions. Solutions for anion interferences were prepared from sodium salts.

General procedure : An aliquot of a standard selenium solution was transferred to 400 ml pyrex beaker. About 40 ml of hydrochloric acid followed by 25 ml of reagent solution were added and the solution was brought to total volume of 100 ml. Reduction of selenious acid to black elemental selenium was carried out on an water bath. The precipitate was immediately filtered off on a sintered glass filter (porosity 4), washed with hot water, alcohol and after drying at 110° was weighed. The results obtained are shown in Table 2.

Results and Discussion

For getting the optimum conditions of the complete reduction, preliminary experiments were carried out. Effects of acidity and time on precipitation was studied in detail. To an aliquot of selenium, varying amounts of hydrochloric acid were added. The study disclosed that the precipitation of selenium is complete from little above 3.0 to about 7.0N hydrochloric acid, approximately 30-70 percent by volume. The results are given in Table 1. It was decided to use 40 ml of the acid in the total volume of 100 ml. The reagent was added in the form of a 4 percent solution in water and 1 ml of the solution is usually sufficient for the precipitation of 5 mg of the metal.

Recovery of seleniums : Solutions containing varying amount of selenium were treated by general procedure. Satisfactory results were obtained for as little as 9.21 mg of selenium with an overall recovery of 99.8 to 100.2%.

(Table 2). Under the conditions employed in these studies, no volatilisation of selenium was evidenced at any time. The procedure involved may be considered as perfectly safe.

TABLE 1—CONDITIONS FOR DETERMINATION OF SELENIUM

Se taken mg	HCl N	Time allowed for pptn h	Se found mg	Recovery %
46.08	2.5	8.0	45.98	99.8
92.16	3.0	2.0	92.32	100.2
92.16	3.5	1.5	92.08	99.9
92.16	4.0	1.0	92.10	99.9
46.08	5.0	1.0	46.01	99.8
46.08	6.0	1.0	45.98	99.8
69.12	7.0	1.0	69.06	99.7

Interference study : A number of cations and anions were tested for a possible interference effect on the method. The effect of these ions is illustrated in Table 3 which refers to a final acidity of 4.0N hydrochloric acid and 1.0 g reagent. At this acidity, interferences from bismuth, arsenic and antimony were masked with tartaric acid. Selenium may be completely separated from copper using EDTA as a masking agent for copper, which, however, does not form a complex with selenite ion. When the metals which form insoluble chlorides are present, the results will be high. Among the anions nitrate, sulphate, phosphate, tartrate, acetate did not interfere.

TABLE 2—RECOVERY OF SELENIUM (HCl, 4N)

Se taken mg	Se obtained mg	Recovery %
9.21	9.20	99.9
11.52	11.49	99.8
18.43	18.40	99.9
23.04	23.01	99.9
46.08	46.04	99.9
69.12	69.19	100.1
92.16	92.10	99.9
115.20	115.32	100.1
138.24	138.10	99.9
184.32	183.96	99.8
[illegible]	200.84	100.2
207.36	207.15	99.9

Determination of selenium and tellurium in an admixture : Synthetic solutions containing definite amounts of selenium (46.08 mg) and tellurium (61.04 mg) were treated by the general procedure using hydrochloric acid. Selenium was completely precipitated in about an hour (Table 4). Good agreement was obtained between the results from the proposed method and those from conventional methods[8]. The procedure is therefore considered suitable for the analysis of selenium-tellurium mixtures.

TABLE 3—INTERFERENCES IN DETERMINATION OF SELENIUM (92.16 MG), WITH N-BENZENESULPHONYLHYDROXYLAMINE (HCl, 4N).

Diverse ion	Amount added mg	Se obtained mg	Recovery %
Cu (II)*	200	92.04	99.9
Ni (II)	100	92.08	99.9
Mg (II)	60	92.10	99.9
Mn (II)	60	92.35	100.2
Zn (II)	100	92.25	100.1
Bi (III) †	50	92.10	99.9
As (III) †	50	92.03	99.8
Sb (III) †	60	92.04	99.9
Cd (II)	100	92.33	100.1
Co (II)	100	92.10	99.9
Tartaric acid	1000	92.15	100.0
EDTA	500	92.33	100.1
Nitrate	1000	92.12	100.0
Sulphate	1000	92.33	100.1

* Masked with EDTA ; † Masked with tartaric acid

Determination of tellurium in the filtrate : Tellurium in the filtrate was determined using thiourea. The filtrate was neutralised by ammonia and heated to about 70° on a water bath. To this a solution containing 3 g of thiourea was added. Heating was continued till tellurium completely settled. This requires not more than 1h. The precipitate was collected, washed and dried. Recovery of tellurium was quantitative in every case (Table 4).

TABLE 4—SELENIUM-TELLURIUM ANALYSIS ON SYNTHETIC SAMPLES (HCl, 4N).

Se taken mg	Te added mg	Se found mg	σ	Te found mg	σ
46.08	61.04	46.02 46.07 46.04 46.14 45.94	0.07	61.16 60.92 61.08 60.88 60.94	0.1

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5-Aryl-6-Mercaptobenzyl-3-Phenyl-4-Phenylimino-2-Thio Tetrahydro-1,3,5-Triazines

N. M. NIMDEOKAR, A. S. MAHAJAN, Y. R. WANI and M. G. PARANJPE*

Department of Chemistry, Nagpur University, Nagpur-10.

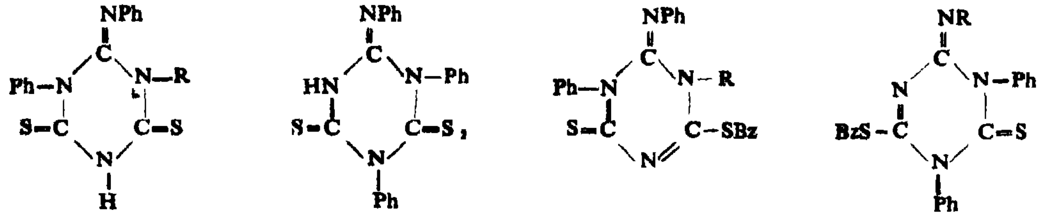
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S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl aryl isothiocarbamides on reaction in boiling benzene medium has been shown to afford 5-aryl-6-mercaptobenzyl-3-phenyl-4-phenylimino-2-thio tetrahydro-1,3,5-triazines. A probable mechanism has been suggested.

INTERACTION of S-chloro-N-phenyl isothiocarbamoyl chloride and aryl thiocarbamides in boiling benzene medium leading to 1,3,5-triazines has been reported earlier[1] and the structure II was suggested for the product of this reaction. The 1,3,5-triazine (IIa) on benzylation with benzyl chloride has been shown to afford its mercaptobenzyl derivative. Therefore, it appeared worthwhile to investigate the reaction of the above isothiocarbamoyl chloride and S-benzyl phenyl isothiocarbamide in boiling benzene medium, which is likely to afford the same mercaptobenzyl derivative reported earlier[1]. Interaction of S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl aryl isothiocarbamides in boiling benzene medium forms the subject of matter of this communication.

But the structure (IVa) viz. 2-mercaptobenzyl-1,5-diphenyl-4-phenylimino-6-thio tetrahydro-1,3,5-triazine was ruled out for this product on the basis of its independent synthesis. The synthesis was performed as follows :

2-S-Benzyliso-4-S-ethyliso-1,5-diphenyl biuret (VIa), (obtained by the reaction of 2-S-benzyliso-1,5-diphenyl-4-thiobiuret (V)[3,4] and ethyl iodide in boiling ethanol followed by basification with dilute aqueous ammonia), on reaction with phenyl isothiocyanate in acetone medium and subsequent cyclisation, eliminated ethyl mercaptan and formed IVa. (Schem 1).



I II III IV

where R = (a) phenyl, (b) *p*-tolyl and (c) *p*-chlorophenyl

The reaction (where aryl = phenyl) afforded a solid, $C_{28}H_{22}N_4S_2$, m.p. 136°, accompanied by evolution of hydrogen chloride. The yield of the product could be increased appreciably when the ratio of the reactants was 2 : 1 molar proportion.

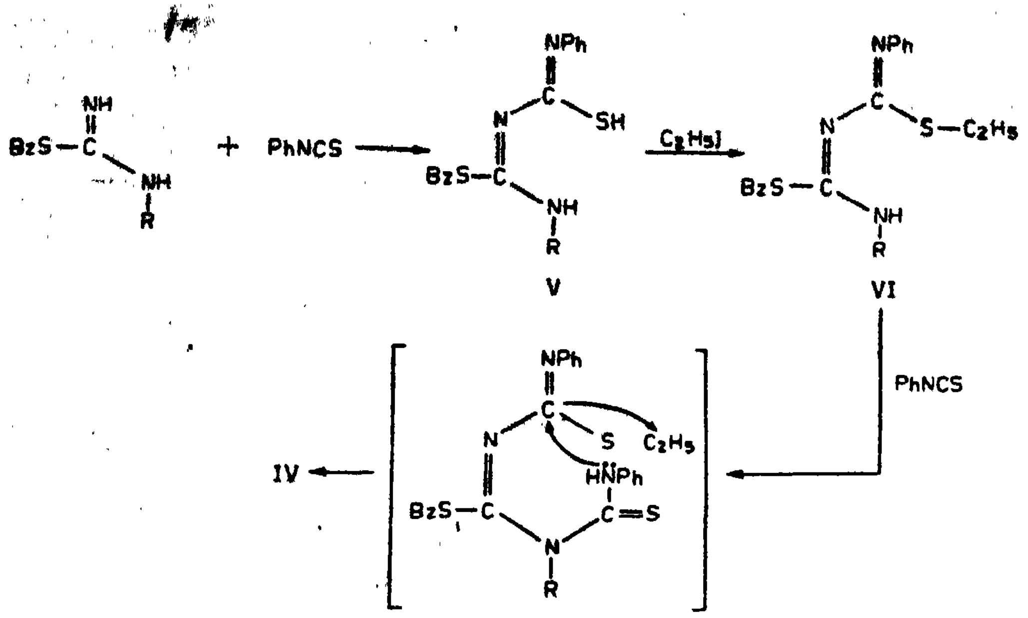
The product was found stable to hot alcoholic ammoniacal hydrogen sulphide and 4% boiling aqueous alkali. It was not desulphurised by hot alkali plumbite solution. Its IR spectrum indicated the presence of C=S, N-C=N and S-CH_2Ph bands and also an isotrizine structure[2]. As expected a ring -NH band was not noticed in spectrum.

On the basis of above facts the product $C_{28}H_{22}N_4S_2$ appears to be most probably a mercaptobenzyl isotriazine derivative for which two formulations IIIa or IVa are possible.

The structure 6-mercaptobenzyl-3,5-diphenyl-4-phenylimino-2-thio tetrahydro-1,3,5-triazine (IVa) therefore, most probably represents the product with m.p. 136°.

It is evident from the reaction that two moles of S-chloro-N-phenyl isothiocarbamoyl chloride reacts with one mole of S-benzyl phenyl isothiocarbamide with loss of a sulphur atom. This sulphur was not eliminated as an elemental sulphur[1], but most probably as sulphur halide.

As expected, the compound with m.p. 136° was found identical in all respects with the free base of mercaptobenzyl derivative reported in our earlier communication[1].



Where R = (a) phenyl (b) p-tolyl

Scheme 1

On extending the reaction of S-chloro-N-phenyl isothiocarbamoyl chloride to S-benzyl *p*-tolyl and *p*-chlorophenyl isothiocarbamides under the similar reaction conditions the related product IIIb and IIIc respectively have been isolated.

The compound IVb (where R=*p*-tolyl) was also ynthesised by procedure analogous to that for IVa by taking S-benzyl *p*-tolyl isothiocarbamide in place of -benzyl phenyl isothiocarbamide.

As the reaction product of S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl phenyl isothiocarbamide in boiling benzene medium was identical with the free base of mercaptobenzyl derivative of 1,3,5-triazine described in our earlier work[1], structure IIIa appeared more suitable for the product and not IVa as suggested earlier. Similarly, the structure I and not II will be more appropriate for the reaction products of -chloro-N-phenyl isothiocarbamoyl chloride and aryl thiocarbamides in boiling benzene medium.

Mechanism of Reaction :

The mechanism of formation of III has been investigated in detail and two distinct intermediate stages have been isolated.

For example, formation of IIIa (where R=phenyl) takes place as follows :

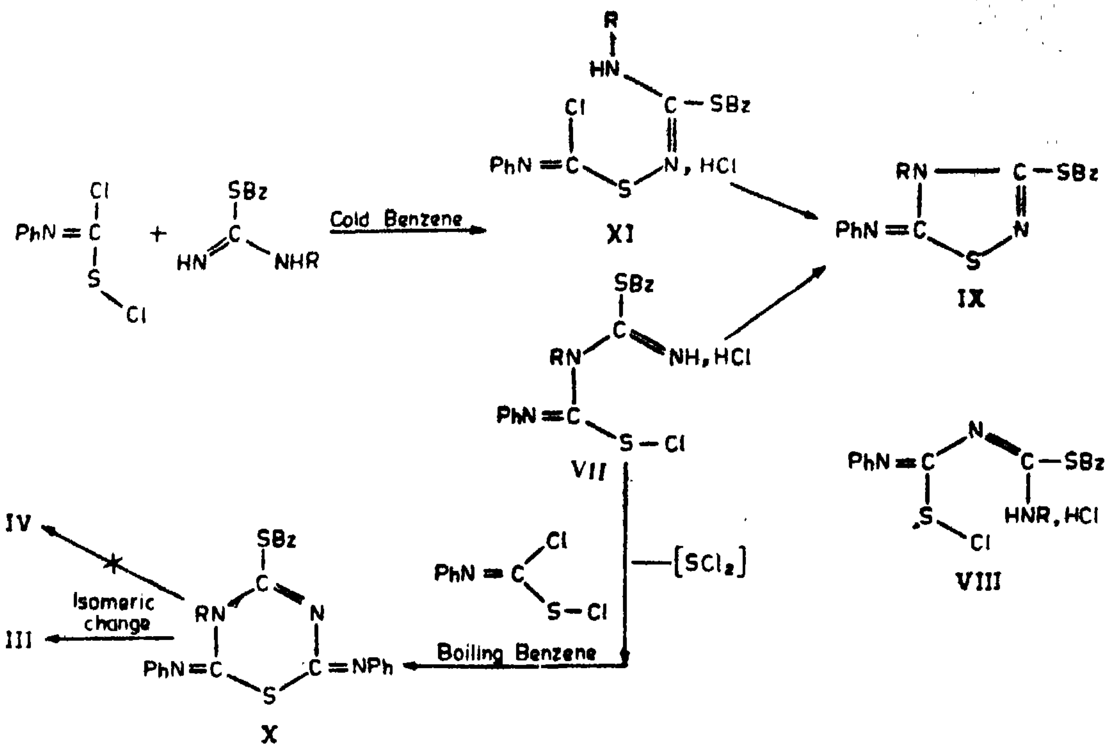
One mole of S-chloro-N-phenyl isothiocarbamoyl chloride, when reacts with one mole of S-benzyl phenyl isothiocarbamide in cold benzene medium gives an unstable intermediate product[5] (VIIa). The structure (VIIIa) for unstable product has been ruled out because this on ring closure cannot give 4-aryl-3-mercaptobenzyl-5-phenylimino-1, 2, 4-thiadiazolines IXa. The more structure XIa cannot be ruled out for this product but formation of IIIa from this will be a multistep process.

The unstable product (VIIa) on reaction with a fresh mole of S-chloro-N-phenyl isothiocarbamoyl chloride in refluxing benzene medium, eliminated hydrogen chloride and a clear solution is obtained. On distilling out benzene, a semisolid mass was left, which on trituration several times with petroleum ether converted into a low melting unstable solid, m.p. 65°. This unstable solid was most probably 2,6-diphenyl-4-mercaptobenzyl-3-phenyl tetrahydro-1, 3, 5-thiadiazine intermediate (Xa). Because on treatment with alcohol it gave IIIa, m.p. 136°, identified on the basis of undepressed m.m.p. with IIIa obtained by the reaction of S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl phenyl isothiocarbamide directly.

The mechanism of the reaction is shown in scheme 2.

The presence of SCl_2 however, could not be established. This might be due to its high reactivity towards moisture.

Similar types of intermediate stages VIIb, VIIc and Xb and Xc have been isolated in the stepwise reactions of S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl *p*-tolyl and S-benzyl *p*-chlorophenyl isothiocarbamides also.



Where R = (a) phenyl (b) p-tolyl (c) p-chlorophenyl

Scheme 2

Experimental

The required S-chloro-N-phenyl isothiocarbamoyl chloride was prepared by the method described earlier[6]. The S-benzyl aryl isothiocarbamides have been prepared by the benzylation of an appropriate aryl thiocarbamide followed by basification with dilute aqueous ammonia.

1. *Interaction of S-Chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl aryl isothiocarbamides in boiling benzene medium.*

Details of a typical experiment (where aryl=phenyl) are as follows :

When S-chloro-N-phenyl isothiocarbamoyl chloride (25 g) and S-benzyl phenyl isothiocarbamide (12 g) were allowed to react in refluxing benzene (100 ml) for three hours, evolution of hydrogen chloride was observed. On distilling out benzene a syrupy mass was left behind which on repeated washing with petroleum ether afforded a semisolid. The semisolid on treatment with cold ethanol dissolved and immediately a solid product was separated (18 g)[7] ; crystals from aqueous acetone/acetic acid, m.p. 136° (Found : C, 69.75 ; H, 4.40 ; N, 11.67 ; S, 13.23. $C_{28}H_{22}N_4S_2$ requires ; C, 70.29 ; H, 4 60 ; N, 11.71 ; S, 13.38°/₀).

This product was found stable to hot alcoholic ammoniacal hydrogen sulphide and 4°/₀ boiling aqueous alkali. It was not found desulphurisable when boiled with alkali plumbite solution. On heating odours of benzyl mercaptan and phenyl isothiocyanate were perceptible.

The IR spectrum of this compound showed the presence of C=S (1164 cm^{-1}) ; N-C=N (1616 cm^{-1}) ; $S\text{-}CH_2PH$ (1215 cm^{-1}) bands. Another band at (1550 cm^{-1}) was most probably due to 1,3,5-triazine ring system. One more band at 750 cm^{-1} probably indicated the presence of an isotriazine ring[2]. The absence of a band due to cyclic-NH was noteworthy.

On the basis of the above facts this product with m.p. 136° has been assigned the structure 6-mercaptobenzyl-3, 5-diphenyl- 4 -phenylimino-2-thio tetrahydro 1,3,5-triazine (IIa). Another possible structure for this product, i.e. 2-mercaptobenzyl-1,5-diphenyl-4-phenylimino 6-thio tetrahydro-1,3,5-triazine(IVa) has been ruled out on the basis of its independenl synthesis.

S-chloro-N-phenyl isothiocarbamoyl chloride (25 g) also reacted with S-benzyl *p*-tolyl isothiocarbamide (13 g) and S benzyl *p*-chlorophenyl isothiocarbamide (14 g) in refluxing benzene medium in an analogous manner afforded the related products IIIb (10 g) ; m.p. 145° (Found : N, 11.17 ; S, 13.13. $C_{29}H_{24}N_4S_2$ requires ; N, 11.38 ; S, 13.00 % and IIIc (18 g) m.p. 139° (Found : N, 10.76 ; S, 12.27. $C_{28}H_{21}N_4S_2Cl$ requires ; N, 10.92 ; S, 12.48°/₀), respectively.

2. *Synthesis of 2-mercaptobenzyl-1,5-diphenyl-4-phenylimino-6-thio tetrahydro-1, 3, 5-triazine (IVa)*

2-S-benzyl iso-1,5-diphenyl-4-thiobiuret (VIa) was converted into 2-S-benzyliso-4-S-ethyliso-1,5-diphenyl biuret (Va) m.p. 70°, by heating the former (10 g) under reflux with ethyl iodide (6ml) in ethanol (30ml) followed

by basification with dilute ammonium hydroxide. A mixture of Va (5 g), phenylisothiocyanate (3 ml) and acetone (40 ml) was heated under reflux for 5 hours, when evolution of ethyl mercaptan was observed. On evaporation of acetone, a sticky residue was obtained which on repeated washing with petroleum ether afforded a solid (3 g), crystallised from aqueous acetic acid, m.p. 218° (Found: N, 11.53; S, 13.28. $C_{28}H_{22}N_4S_2$ requires; N, 11.71; S, 13.38%).

It was found non-desulphurisable when boiled with alkali plumbite solution. On heating odours of benzyl mercaptan and phenyl isothiocyanate, were quite perceptible. The IR spectrum of this compound showed the presence of C=S (1160 cm^{-1}), S-CH_2Ph (1200 cm^{-1}) and N-C=N (1640 cm^{-1}). It also indicated the presence of two bands at 1575 and 60 cm^{-1}, characteristic of isotriazine ring system[2]. Here also band due to-NH was found absent.

The related compound IVb (where R = *p*-tolyl), m.p. 228° (Found: N, 11.08; S, 13.18. $C_{29}H_{24}N_4S_2$ requires; N, 11.38; S, 13.00%) has also been synthesised by taking S-benzyl *p*-tolyl isothiocarbamide in place of S-benzyl phenyl isothiocarbamide. The synthesised IVb was found completely different from the product (IIIb) obtained directly by the interaction of S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl *p*-tolyl isothiocarbamide (*vide* supra).

Mechanism

(a) *Interaction of S-chloro-N-phenyl isothiocarbamoyl chloride and S-benzyl aryl isothiocarbamides in 1:1 ratio : Formation of VII* :

Details of a typical experiment (where aryl = phenyl) are as follows :

When to a well cooled solution of S-benzyl phenylisothiocarbamide in benzene (24 g in 100 ml) was added gradually a benzene solution of S-chloro-N-phenyl isothiocarbamoyl chloride (25 g in 50 ml) and the mixture maintained around 5° by cooling in freezing mixture, a reaction with evolution of hydrogen chloride was noticed. After standing for several hours, a solid was deposited. The solid was quickly washed several times with benzene followed by petroleum ether, when an unstable product $C_{21}H_{18}N_3S_3Cl,HCl$ (VIIa) was obtained (Found: N, 9.01; S, 14.34. $C_{21}H_{18}N_3S_2Cl$, HCl requires, N, 9.33; S, 14.22%). It was acidic in nature and was found desulphurisable with hot alkali plumbite solution. On heating it decomposed and smell of benzylmercaptan was quite perceptible.

Similarly, S-chloro-N-phenyl isothiocarbamoyl chloride on reaction with S-benzyl *p*-tolyl isothiocarbamide and S-benzyl *p*-chlorophenyl isothiocarbamide under analogous reaction conditions afforded related VIIb m.p. 120° (d) and VIIc m.p. 86° (d).

(b) *Reaction of VII with a fresh mole of S-chloro-N-phenyl isothiocarbamoyl chloride : Formation of X* :

Following are the details of a typical reaction of VIIa with 1 mole of S-chloro-N-phenyl isothiocarbamoyl chloride :

A mixture of VIIa (35 g) and S-chloro-N-phenyl isothiocarbamoyl chloride (25 g) was refluxed for 2 hours. During the progress of heating gradually VIIa went into solution and evolution of hydrogen chloride was observed. After distilling out benzene, a sticky semisolid was obtained, which on trituration several times with petroleum ether and standing turned into a reddish brown solid (22 g), m.p. 62° (d). This solid was purified by redissolving in benzene and precipitating it with petroleum ether, m.p. 65° (d) (Found: N, 10.84; S, 12.48. $C_{28}H_{22}N_4S_2$ requires; N, 11.62; S, 13.28%). It was found unstable when exposed to atmosphere. This was expected to be 2,6-diphenyl-4-mercaptobenzyl-3-phenyl tetrahydro-1, 3, 5-thiadiazine (Xa). This on treatment with ethanol first dissolved and then reprecipitated as stable white solid, crystallised from dilute alcohol, m.p. 136°. This was found identical with the reaction product, m.p. 136° (IIIa), obtained directly by the reaction of S benzyl phenyl isothiocarbamide and S-chloro-N-phenyl isothiocarbamoyl chloride.

Similarly VIIb and VIIc on further reaction with S-chloro-N-phenyl isothiocarbamoyl chloride afforded the related Xb and Xc m.p. 53° (d) and 71° (d) respectively. As expected both were very unstable. These also on treatment with aqueous ethanol afforded IIIb and IIIc respectively.

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Synthesis and Spectral Studies on Mono- and Trialkyltin and Triphenyltin(IV) Chelates with Substituted-8-quinolinols†

(Miss) C. D. BARSODE, P. UMAPATHY* and D. N. SEN

National Chemical Laboratory, Poona-8

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Several mono- and trialkyl/triphenyltin(IV)-substituted-8-quinolinols have been synthesised and characterised by their elemental analysis, U. V. and I. R. spectral data. The absorption bands located at Ca. 570 cm^{-1}, 440 cm^{-1} and at Ca. 360 cm^{-1} in the alkyltin(IV) chelates have been assigned to the tin-carbon, tin-oxygen and tin-nitrogen stretching frequencies respectively. The U. V. spectra of these compounds show the presence of chelating oxine groups.

A few mixed chelates of the type $R_2SnL_1L_2$ (where HL_1 = 8-quinolinol and HL_2 = a β-diketone, dibenzoylmethane or benzoylacetone) also have been isolated and characterised.

THE ability of organotin moieties to react with potentially chelating ligands to form stable complexes with high coordination is well established. The 8-quinolinol derivatives are classical examples of 5-, 6- and 7-coordinate chelates reported in literature[1-5]. Although most of the conventional techniques namely Mössbauer, I.R. and N.M.R. spectroscopies have been employed as aids in structural investigations,[1,2,6] the geometry of certain of these oxinates is still in doubt. Triphenyltin oxinate has been studied by several investigators and from its U.V. spectral data, in 95% methanol, it was concluded that R_3Sn^+ cations could not form a chelate[7]. However, Okawara and coworkers[8] have found that in anhydrous cyclohexane, triphenyltin oxinate is, indeed, chelated and tin is penta-coordinated. Among the seven-coordinate organotin chelates, mention may be made of phenyltin tristropolonate[9] and butyltintrisoxinate. In continuation of our studies on dialkyltin(IV) substituted-8-quinolinols,[10,11] several stable complexes of mono-and trialkyltin(IV) substituted-8-quinolinols have been synthesised. In addition, dialkyltin(IV) mixed chelates of the type $R_2SnL_1L_2$ (HL_1 = 8-quinolinol and HL_2=a β-diketone) and chloroorganotin chelates, RSnClOx, (HOx=5,7-disubstituted-8-quinolinol) have been isolated in pure state. The salient features of the U. V. spectra of these compounds along with dialkyltin(IV)bis-substituted-8-quinolinolates, the I. R., P.M.R. and mass spectral data for some of the organotin(IV) chelates are presented in this paper.

Experimental

The U.V. spectra of all the tin(IV) chelates were recorded (in different solvents) on an Unicam SP 500 spetrophotometer. The I.R. spectra in Nujol mull were recorded on a Perkin-Elmer model 221 spectrophotometer. The P. M. R. spectra were recorded on a Varian T-60 spectrometer operating MC/s with TMS as internal standard. ' spectra of the mixed chelates were recorded 21-110B (USA) Double focussing spectr voltage of 70 eV and a current of 20 milliampe

Triethyltinchloride and ethyltin trichlor prepared according to the methods described b and Vander Kerk[12,13]. Triphenyltin chlorid sample and is used as such.

The trisligand complexes were prepared by a general procedure : To a solution of ethyltint (0.6 g., 0.0025 mole) in alcohol (10 ml.), t (0.0075 mole) in alcohol (30 ml.) was added w rous stirring. Stirring was continued for 15 mt *p*H of the solution was adjusted to ~5.5 with sodium acetate solution. The precipitates were collected on a filter, dried under vacuum further purified by recrystallization from mentioned in Table 1. The triaryl or alk chelates were also obtained in a similar man syntheses of dialkyltin(IV) chelates were elsewhere[10,11].

Mixed chelates : Diethyltin(IV) mixed have been synthesised directly by refluxing dichloride, 8-quinolinol and a β-diketone (d methane or benzoylacetone) in a solvent (al 5-6 hrs. and by adjusting the *p*H of the mixed to ~5.5. The isolated solids were further p several recrystallisations. The physical and data for the organotin(IV)-substituted oxi presented in Tables 1-4.

† N. C. L. Communication No. 2092
* Author to whom correspondence should be addressed.

Results and Discussion

U. V. Spectra : The bands of 8-hydroxyquinolinolate anion have been assigned by several workers[14-17] and according to these authors the absorption band appearing at 322 nm is the low energy transition, La and the one at 317.5 nm is the high energy transition, ^1L_b. In the U.V. spectra of alkyltin(IV) substituted oxinates R_3SnL, R_2SnL_2, $RSnCl(L)_2$ and $RSnL_3$ (where L=anion of a substituted oxine) two well seperated bands at relatively low energy, one in the region 360-400 nm and another at Ca. 340 nm. are observed. From the position and intensity, the band at 360-400 nm is supposed to be the ligand band strongly shifted from its original position (^{1}La). The other band at Ca.340 nm is in the same position as the usual ^1L_b band and is found to be insensitive to changes in substitutent or solvent. The shift to longer wave length of 320 nm. absorption band suggests that, in solution, the organotin compounds listed in Table 2 contain a chelated(substituted oxinato)ligand.[14-16,18,19] The other band which is weak in compounds 8 and 15 but intense in 1 to 7, 9 to 14 and 16 to 21 is also observed in the spectra of other metal oxinates.[16-18]

The chelates with formula R_3SnL form a new class of compounds containing a penta-coordinated tin atom and the chelates $RSnL_3$ are probably having trigonal bipyramidal configurations.[2,21] There has been some disagreement concerning the structure of Ph_3SnOX and Ruddick and Sams[2,20] from their studies on 119Sn Mössbauer spectra of organotin(IV) oxinates in applied magnetic fields have concluded that Ph_3SnOx is five coordinate.

The magnitude of the shift of 320 nm absorption band in the U. V. spectra of chelated oxinato complexes has been correlated with the complex stability[16,22]. If the relation between the band shift and stability is applicable in these chelates the following sequence of stability in solvents, such as, cyclohexane, methanol can be obtained from the table 4.

$$R_2SnL_2 \simeq RSnXL_2 > RSnL_3 > R_3SnL.$$

It is observed that the shift of the ligand band to longer wave lengths is, in general, more in organotin substituted oxinates, compared to the shift reported for the corresponding organotin oxinates. The separation between ^{1}La and ^{1}Lb transitions of certain oxinato complexes has been used as a rough measure of the π bonding between cations and the ring, since the relative positions of the two transitions are insensitive to changes in σ bonding by cations[23].

Although the U.V. spectrum of $(C_2H_5)_3Sn$ (dibromo Ox) in cyclohexane indicates clearly the presence of chelated oxine ligand, in aqueous methanol, the 390 nm band is reduced in intensity and a strong band is observed at Ca.320 nm. This suggests that the Sn-N bond of triorganotin oxinates becomes weaker in polar solvents. The changes observed in methanol may be ascribed to solvolysis.[22,24]

I. R. spectra : In the I. R. spectra of 5-, 7- and 5,7-disubstituted-8-quinolinols a broad, medium to weak intensity band at Ca.3200 cm^{-1}, which may be associated with an inter/intramolecularly bonded OH vibration, is observed. In the solution spectra of several substituted-8-quinolinols, Badger and Moritz[26] observed such a band at Ca.3400-3350 cm^{-1}. The medium intensity band present in the ligands at Ca.1410 cm^{-1} can be ascribed to the phenolic OH in plane deformation vibration coupled with C-O Str. mode. The second coupled mode expected at Ca. 1200 cm^{-1} could be located in all substituted-8-quinolinols. However, the OH out of plane deformation vibration at Ca.850 cm^{-1} could not be located clearly due to ligand absorptions. The C=N str. frequency somewhat coupled with pyridine ring vibration appears as a strong band in substituted-8-quinolinols at Ca.1580 cm^{-1}. In dialkyltin(IV) chelates and in mono- or triorganotin(IV) chelates, however, this band shifts[26] to Ca.1570 cm^{-1} and to 1560 cm^{-1} respectively. The characteristic[27] c-o stretching frequency at $\diagdown$C-O-M$\diagup$ site is observed at $\sim$1100 cm^{-1} in the spectra of all substituted-8-quinolinols. The bands observed at Ca.1280, 1190, 1150 cm^{-1} spectra of the compounds may be attributed to in the substituted pyridine ring vibrations[28].

In the spectra of organotin(IV) compounds except in the chelates of 5-nitro-7-bromo-8-quinolinol, strong bands characteristic of Sn-alkyl groups are observed which are not present in the spectra of the ligands. In diethyltin(IV) compounds particularly, the asymmetric CH_3 -deformation of Sn-Et can be located at Ca.1440 cm^{-1}. The symmetric mode, however, cannot be located precisely, since this region ($\sim$1180 cm^{-1}) is masked by ligand absorptions. In diethyltin dialkoxides and other dialkyltin dialkoxides, $Et_2Sn(OR)_2$, the asymmetric and symmetric CH_3-deformation modes of Sn-Et are reported at 1456 cm^{-1} and at 1188 cm^{-1} respectively[29]. Another new characteristic band observed in the spectra of organotin(IV) compounds is the CH_3-Sn rocking mode at Ca.740 cm^{-1}. Methyl compounds of Group IV elements are usually characterised by the presence of a very strong band between 700-900 cm^{-1} which has been assigned to a methyl rocking mode[30]. The band present in methyltin compounds at $\sim$70 cm^{-1} may arise due to CH_3-Sn rocking mode and in ethyl and other alkyltin compounds due to CH_2-Sn. In diethyltin dichloride CH_2-Sn and C-Me rocking modes occur at 688 and 723 cm^{-1} respectively in the solid state (Nujol mull), but in solution the weak higher frequency band is no longer observed and the Sn-CH_2 rock of dichloride and the dialkoxides[29] occur at 681 cm^{-1}. Dillard and Lawson[31], however, have assigned the 680 cm^{-1} band of tetraethyltin to the CH_2-C rock and in triethylmethyltin assigned bands at 670 cm^{-1} to CH_2-C rock and the 728 cm^{-1} band to the CH_3-rock. In 5,7-dichloro- and 5,7-dibromo-8-quinolinol chelates, however, the unequivocal assignment of this band to CH_3-Sn rock becomes difficult. since C-Cl and C-Br absorptions are reported to occur at 750-700 cm^{-1} and at 700-650 cm^{-1} respectively[32]. In organotin(IV)

TABLE 1—THE ANALYTICAL DATA FOR ORGANOTIN (IV) SUBSTITUTED OXINATES

Compound	Crystallising solvent	M. P. (°C)	Yield (%)	Analyses (%)[a] C	H	N	Sn
1. Tris (5,7-dichloro-8-quinolinolato) ethyltin (IV)[c]	Pet. ether (60-80°)	161-63	82.2	44.09 (44.24)	2.61 (2.19)	5.34 (5.39)	14.65 (15.15)
2. Tris (5,7-dibromo-8-quinolinolato) ethyltin (IV)	Methanol	178-80	96.5	32.14 (32.68)	2.36 (1.81)	3.63 (4.01)	11.01 (11.24)
3. Tris (5-nitro-8-quinolinolato) ethyltin (IV)	Benzene	>250 (decmp.)	66.6	49.47 (48.73)	3.98 (4.06)	11.26 (11.76)	16.16 (16.61)
4. Tris (5,7-dinitro-8-quinolinolato) ethyltin (IV)	DMF + water	229-30	25.59	41.30 (40.97)	3.01 (2.01)	14.33 (14.79)	14.43 (13.98)
5. Chlorobis (5,7-dichloro-8-quinolinolato) ethyltin (IV)	Pet. ether (60°-80°)	120-21	59.2	38.90 (39.41)	2.90 (2.15)	3.86 (4.61)	19.95 (19.48)
6. Chlorobis (5,7-dibromo-8-quinolinolato) ethyltin (IV)	Benzene	212-3	85	31.57 (30.50)	2.60 (2.08)	3.79 (3.56)	14.98 (15.08)
7. (5,7-Dibromo-8-quinolinolato) triethyltin (IV)[c]	Carbon tetrachloride	70-73	—	36.09 (35.48)	3.74 (3.69)	2.34 (2.76)	23.89 (23.93)
8. (5,7-Dibromo-8-quinolinolato) triphenyltin (IV)	Cyclohexane	176-8	70	50.18 (49.76)	3.55 (3.38)	2.86 (2.15)	18.12 (18.24)
9. (5,7-dichloro-8-quinolinolato) triphenyltin (IV)	Pet-ether (60°-80°)	123-24	80	56.98 (57.69)	3.68 (3.38)	2.34 (2.49)	20 32 (20.65)
10.. (5-Nitro-8-quinolinolato) triphenyltin (IV)	,,	162-64	74.3	59.63 (60.19)	3.95 (3.71)	6.19 (5.19)	21.93 (22.03)
11. (5,7-Dinitro-8-quinolinolato) triphenyltin (IV)	Methanol	235-6	—	55.55 (55.01)	3.11 (3.26)	7.70 (7.36)	29.65 (20.31)
12. (8-Mercapto-quinolinolato) triphenyltin (IV)	Benzene	167-68	—	63.93 (63.50)	4.34 (4.12)	2.42 (2.74)	23.17 (23.25)
13. (8-Quinolinolato) (1,3-diphenyl-propanedionato)-diethyltin (IV)	Pet. Ether (60-80°)	71-73	66.1	60.99 (61.66)	5.44 (4.97)	2.05 (2.50)	21.60 (21.83)
14. (8-Quinolinolato)(1-phenyl-1,3-butanedionato)-diethyltin (IV)[b]	Pet. ether or Alcohol	138-9°	—	57.58 (57.30)	4.92 (5.19)	2.8 (2.91)	24.42 (24.65)

a Calculated values are given in parentheses

b This compound was also prepared by refluxing bis (8-quinolinolato) diethyltin and b°nzoylacetone in alcohol for 5 hrs.

c The starting materials, $(C_2H_5)_3SnCl$ and $C_2H_5SnCl_3$ were purified by fractional distillation -
Anal. found $(C_2H_5)_3SnCl$: Sn, 48.92 (49.21) ; Cl, 14.31 (14.73) ; for $C_2H_5SnCl_3$: Sn, 47.12 (46.81) ; Cl, 41.46 (42.01%).

TABLE 2—ULTRAVIOLET ABSORPTION SPECTRA OF 8-QUINOLINOLS

Compound	Solvent	λ_{max} (nm)	ϵ ($M^{-1}cm^{-1}$) $\times 10^{-3}$
1. 8-Quinolinol*	$CHCl_3$	320	2.70
2. 8-Quinolinol, 5,7-dichloro	$CHCl_3$	337	3.00
3. 8-Quinolinol, 5,7-dibromo*	$CHCl_3$	337	3.00
4. 8-Quinolinol, 5-nitro	Methanol	340	9.26
5. 8-Quinolinol, 5,7-dinitro	Dioxane	355	—
6. 8-Mercaptoquinoline	Methanol	340	1.37

* λ_{max} for these compounds was reported.

TABLE 3—P. M. R. SPECTRAL DATA FOR THE MIXED CHELATES (SOLVENT : CARBONTETRACHLORIDE).

Compound	Ring protons (τ) (include—CH of the β-diketone)	Ethyl-protons	(τ)
1. $(C_2H_5)_2Sn(Ox)$-$(C_6H_5COCHCOC_6H_5)$	1.5 , 2.03 2.57, 2.93 3.15, 3.6	8.0	8.83
2. $(C_2H_5)_2Sn(Ox)$-$(C_6H_5COCHCOCH_3)$	1.57, 2.0 2.40, 2.58 3.00, 3.17	7.5	8.83

TABLE 4—ULTRAVIOLET ABSORPTION SPECTRA OF ORGANOTIN (IV) SUBSTITUTED OXINATES

Compound	Solvent	λ_{max} (nm.)	ϵ $(M^{-1}\ cm^{-1}) \times 10^{-3}$
1. $(C_6H_5)Sn(Ox)_3$ +*	Benzene	385	6.19
2. $(C_6H_5)Sn$(5,7-dichloro-Ox)	Methanol	390 343	6.49 5.90
3. $(C_6H_5)Sn$(5,7-dibromo-Ox)$_3$	,,	395 340	6.13 5.75
4. $(C_6H_5)Sn$(5-nitro-Ox)$_3$	Methanol + dioxane	390 330	8.26 8.82
5. $(C_6H_5)Sn$(5,7-dinitro-Ox)$_3$	dioxane	385 300	1.31 1.08
6. $(CH_3)SnCl(Ox)_2$*	Benzene	383	4.07
7. $(C_6H_5)SnCl$(5,7-dichloro-Ox)$_2$	Methanol	398 330	3.92 3.95
8. $(C_6H_5)SnCl$(5,7-dibromo-Ox)$_2$	,,	398 340	4.62 2.30
9. $(CH_3)_2Sn(Ox)_2$	Benzene	380	4.86
10. $(C_6H_5)Sn(Ox)_2$	Methanol	375	3.48
11. $(C_4H_9)_2Sn(Ox)_2$	,,	375	7.8
12. $(C_8H_{17})_2Sn(Ox)_2$	,,	375	29.63
13. $(C_6H_5)_2Sn$(5,7-dichloro-Ox)$_2$	Methanol + $CHCl_3$	390 340	6.95 6.02
14. $(C_6H_5)_2Sn$(5,7-dibromo-Ox)$_2$	,,	395 345	6.32 2.66
15. $(C_6H_5)_2Sn$(5-nitro-Ox)$_2$	Methanol	410 320	4.27 1.18
16. $(CH_3)_3SnOx$*	Cyclohexane	362	2.50
17. $(C_2H_5)_3Sn$(5,7-dibromo-Ox)	,, Methanol	390 350 400 330	2.92 2.42 3.92 3.95
18. $(C_6H_5)_3SnOx$*	Cyclohexane	368	2.44
19. $(C_6H_5)_3Sn$(5,7-dichloro-Ox)	,,	385 340	3.93 2.31
20. $(C_6H_5)_3Sn$(5,7-dibromo-Ox)	,,	395 340	4.04 2.82
21. $(C_6H_5)_3Sn$(5-nitro-Ox)	$CHCl_3$	340	9.56
22. $(C_6H_5)_3Sn$(8-S-quinoline)		360	—
23. $(C_6H_5)_2Sn$(Ox)(DBM)	Cyclohexane	~390, 337	—
24. $(C_6H_5)_2Sn$(Ox)(BA)	,,	~390, 337	—

* λ_{max} for these compounds was reported
+HOx = 8-quinolinol.

chelates of 5-nitro-8-quinolinol and 5,7-dinitro-8-quinolinol strong ligand absorption bands are found in this region (750-770 cm^{-1}).

The I. R. spectra of triphenyltin(IV) substituted-8-quinolinols show a strong absorption band at 1070-80 cm^{-1}. Henry and Noltes[23] and Poller[24] have shown that the band at 1065 cm^{-1}, in compounds of the general type, $(C_6H_5)_xSnA_{4-x}$(X=a diversity of chemical types) is characteristic of the phenyltin group and has a diagnostic value. This band has also been noted by a number of other workers and assigned to a C-H in plane deformation vibration[25].

The strong broad band observed at Ca.450 cm^{-1}, in the spectra of organotin(IV) substituted-oxinates has been assigned to tin-oxygen stretching vibration on the basis of corresponding assignments in organotin-8-quinolinolates[1]. The other new band observed at Ca.370 cm^{-1} has been assigned to ν(Sn-N). modes[26]. The Sn-C stretching frequency is observed as a strong band in the spectra of all the mono- and tri-substituted oxinates in the region 560-580 cm^{-1}.

Mixed chelates: The proton chemical shifts of the compounds (8-quinolinolato) (1-phenyl-1,3-butanedionato)diethyltin(IV) and (8-quinolinolato)(1,3-diphenylpropanedionato)-diethyltin(IV) given in Table 3 are comparable with the corresponding shifts in the diphenyl tin mixed chelates, $(C_6H_5)_2Sn(Ox)$ $(C_6H_5COCHCO\text{-}C_6H_5)$ reported by Westlake and Martin[27]. The observed intensity ratios of ethyl and ring protons (include =CH of the β-diketone) agree fairly well with the calculated values (2:3 and 2:3.4) in $(C_2H_5)_2Sn(Ox)(C_6H_5COCHCOCH_3)$ and in $(C_2H_5)_2Sn(Ox)\text{-}(C_6H_5COCHCOC_6H_5)$, respectively. In the I. R. spectra of the mixed chelates $(C_2H_5)_2Sn(Ox)(DBM)$ and $(C_2H_5)_2Sn(Ox)$ (BA) a medium intense peak is observed at$\sim$1230 cm^{-1} which can be ascribed to a CH in-plane bending vibration in analogy with the reported[28] CH in plane bending frequency in copper and nickel chelates of dibenzoylmethane and benzoylacetone. The band observed at Ca.1500 cm^{-1} in the spectra of these organotin(IV) mixed chelates can be assigned to the phenyl ring vibrations. The asymmetric CH_2-deformation of Sn-Et, a characteristic band of Sn-alkyl groups[29] could be located at 1450 cm^{-1}. The new frequency observed in these chelates at 750 cm^{-1} is due to the Sn-CH_2 rocking mode[30].

In the mass spectra of organotin(IV) mixed chelates, fragmentation path-ways corresponding to the presence of both the ligands are observed. In the spectrum of $(C_2H_5)_2Sn(Ox)$ (BA), only a weak molecular ion is observed at m/e 484. Successive losses of ethyl radicals from the parent ion result in the formation of the low valent species SnL_1L_2 (m/e 425) (where L_1 =Ox and L_2 = BA). Another mode of fragmentation of the molecular ion appears to be the loss of a methyl redical followed by the elimination of ethylene (m/e 441). The appearance of a peak at m/e 158 according to the scheme reported earlier[10] confirms this mode of dissociation. Although the molecular ion is not observed in the spectrum of $(C_2H_5)_2Sn(Ox)(DBM)$, loss of a methyl radical followed by ethylene elimination can be observed at m/e 502. A weak peak observed at m/e 158 supports this mode of disintegration. The other low valent species, SnL_1^+, SnL_2^+ (in abundance), $C_2H_5SnL_1$ and fragment ions corresponding to 8-quinolinol and β-diketones[30] are also observed in the spectra of both the mixed chelates.

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Study of Ion-Solvent Interaction in Ethylene Carbonate from Viscosity Data

R. GOPAL* and S. SINGH

Chemistry Department, Lucknow University, Lucknow

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Ion-solvent interaction of some tetraalkylammonium and common ions in ethylene carbonate (EC) has been studied from the viscosity data in this communication. The study indicates that the tetraalkylammonium ions are not solvated while the common ions are and their solvation appears to vary inversely as the radius of the ion; the structure of the solvent appears to remain unaffected beyond the solvation layer in presence of these ions.

IN continuation with the earlier studies on ion-solvent interaction of the tetraalkylammonium and alkali metal halides in dimethylsulphoxide (DMSO)[1,2] and propylene carbonate(PC)[3,4], the work has now been extended to ethylene carbonate (EC) which, although is similar to these liquids in having no hydrogen-bonding interaction, has a high dielectric constant (85.81)[5] which would ensure complete ionization of electrolytes when dissolved in it. It has also a considerable liquid range. Although some studies on viscosity of electrolytes have been reported[6], a detailed investigation is still lacking. It is proposed to undertake a study of ionsolvent interaction of some tetraalkylammonium and common salts from the point of view of viscosity in this communition.

Experimental

Ethylene carbonate (Fluka, purum) was fractionally crystallised three times and the sample thus obtained was distilled under reduced pressure. The middle fraction of the distillate was collected in a dark coloured bottle and kept in a dry box. The sample was found to melt sharply at 36.5° and its electrical conductance was of the order of 10^{-6} mho.

The tetraalkylammonium iodides (DPI, U.S.A.) and common salts (BDH, AR) were purified in the usual manner. Solutions were prepared on weight basis and volume concentration was obtained from the corresponding density. The experimental procedure for measuring density and viscosity, the equipment used and precautions are the same as described earlier[8].

Results and Discussion

From the data thus obtained viscosity was calculated, and the specific viscosity

$\Psi = \frac{\eta - \eta_0}{\eta_0}$ was obtained and $\Psi/\sqrt{C}$ calculated. The $\Psi/\sqrt{C}$ vs $\sqrt{C}$ curves for different salts for different temperatures were drawn.

The solute-solvent interaction in ethylene carbonate was examined using the well known Jones and Dole viscosity equation[7], namely,

$$\frac{\eta - \eta_0}{\eta_0\sqrt{C}} = \Psi/\sqrt{C} = A + B\sqrt{C}$$

the values of coefficient B obtained from the $\Psi/\sqrt{C}$ vs $\sqrt{C}$ plots in different cases are given in table 1.

TABLE 1 : B VALUES OF SALTS AT DIFFERENT TEMPERATURE IN EC

Salts	B values at 40°	45°	50°	55°
Me_4NI	0.571	0.560	0.551	0.543
Et_4NI	0.712	0.712	0.702	0.711
Pr_4NI	0.794	0.801	0.793	0.795
Bu_4NI	0.920	0.923	0.910	0.912
Pen_4NI	1.042	1.049	1.051	1.050
Hex_4NI	1.203	1.203	1.193	1.202
Hep_4NI	1.302	1.321	1.312	1.313
$LiI.H_2O$	0.850	0.804	0.770	0.750
NaI	0.821	0.801	0.791	0.750
KI	0.652	0.638	0.652	0.669
RbI	0.581	0.574	0.576	0.568

Referring to table 1, it may be observed that the effect of temperature on the B-coefficient appears to be very little in this solvent as in most other non-aqueous aprotic solvents with little or no molecular association due to the absence of hydrogen bonding in them; some

slight, erratic and haphazard changes may be ignored. Thus from the temperature independence of B it appears that the structure of the solvent remains unaffected in presence of these salts.

The variation in the value of B with the radius of the ion may next be examined to see if this would be of any help. Although this variation may be observed in table 1, it is made more explicit from Fig. 1 in which B value for salts has been plotted against radius of the cation. It may be remarked that since I^- is common to all these salts, variation in B with the radius may be assumed to be due to the cation only.

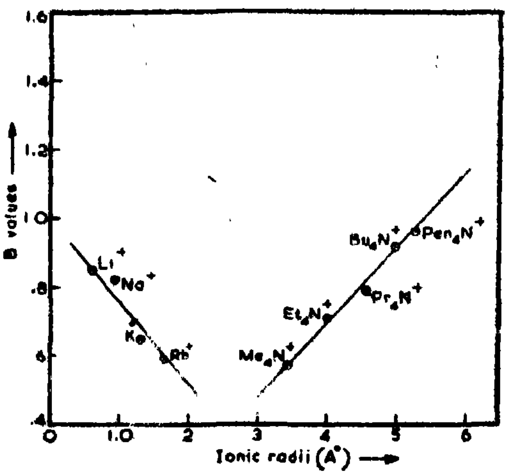


Fig. 1. B Vs Ionic radii plot in E C

It may be noted from Figure 1 that for the salts containing R_4N^+ ions, B value is larger, the larger the cation which indicates that the electrostatic ion-solvent interaction, if at all, is very weak in these cases and resistance to the movement of the ion in solution depends upon the size (i.e. radius) of the bare ion only. Reverse appears to be the case with the common salts containing small compact cations for which B decreases with the increasing size of cation. Apparently, the high charge density on the smaller cations gives rise to strong electrostatic ion-solvent interaction in solution which does not appreciably change within small temperature range of the present investigation, and hence it is not shown up as the change in the value of B when the temperature changes. The smaller the ion, the stronger the ion-solvent dipole interaction and the larger the size of the solvated ion in solution and the larger the value of B. Thus the result of this investigation lead one to conclude that while the R_4N^+ ions do not appear to be solvated in EC, the alkali metal ions are appreciably solvated, their solvation varying inversely as the radius of the cation.

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Galvanostatic and Chronopotentiometric Study of the Oxidation of Ethyl Alcohol at Platinized Platinum Electrode*

K. VENKATESWARA RAO and C. B. ROY

Department of Chemistry, Indian Institute of Technology, Kharagpur-721 302.

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The oxidation of ethyl alcohol was studied at platinized platinum electrode in acid medium using Galvanostatic method at steady-state condition and chronopotentiometric method. The data indicate that the process is activation controlled. The system was studied at different temperatures and the energy of activation was found to be 14 K. cal mole^{-1}. The rate was found to depend on concentration of ethanol up to the concentration of 1 5*M* and above this, the rate was independent of concentration. The observed Tafel slope of 120 mv per decade was not dependent either on concentration of ethanol or temperature up to the potential 0.8V. Potential oscillations were observed at higher potentials. The exchange current density was found to be about 10^{-6} A cm^{-2} at 28°. *p*H was found to have no effect on the rate.

Chronopotentiometric results were interpreted as that two electrons were involved in the oxidation process and the oxidation of the adsorbed species was the rate determining step. The effect of molybdate ion and the product acetaldehyde on the rate was studied. A probable mechanism was put forward for the electrochemical oxidation of ethanol.

THE work reported here is a part of the study of the basic mechanism of oxidation of liquid organic compounds which can be used in fuel cells. In the present paper the oxidation of a typical fuel, ethanol on platinized platinum in sulphuric acid was studied.

Several studies have been reported on the oxidation of ethanol at platinum during recent years[1-6]. Rightmore et al.[1] proposed a fast chemisorption step involving charge transfer followed by a rate determining electrochemical step.

$$CH_3\,CH_2OH \rightleftharpoons CH_3\,CHOH_{ad} + H^+ + e$$

$$CH_3\,CHOH_{ad} \xrightarrow{\text{r.d.s.}} CH_3\,CHO + H^+ + e$$

Gileadi and Pierzma[2] derived kinetic equations assuming that the first step is in pre-equilibrium but were unable to explain all the reported experimental results. They assumed that, poisoning of the surface at higher potential was due to the formation of oxide layer on the surface of the electrode. Liang et al.[3] deduced the initial chemisorption step was rate determining step. Blake et al.[4] in their mechanistic studies discussed all the possible mechanisms suggested by Rightmore, Frumkin, Brumer and finally Bockris' widely accepted generalized mechanism for a variety of anodic oxidations, especially hydrocarbons, in the light of their findings. Podlovchenko et al.[5] postulated that if ethanol is introduced at an electrode registering a potential in the double layer, the scission of the bond occurs. They proposed a possible mechanism which involved a number of free radicals in the reaction scheme.

In the present paper Galvanostatic and Chronopotentiometric methods were used for the determination of mechanism; the latter method, was used for the determination of the type of the reaction, number of electrons involved in the oxidation process and fractional coverage of the adsorbed species at open circuit potential. The effect of molybdate ion (Mo^{+6}) as a catalyst (redox catalyst) on the rate was studied using Galvanostatic and Chronopotentiometric methods. The effect of the oxidation product of ethanol namely, acetaldehyde was studied on the rate.

Experimental

The electrochemical cell used was described previously[6]. The details of the Galvanostatic technique were given elsewhere[7]. The test electrode and the auxiliary electrode consisted of platinum foil of 2 cm^2 geometric area. The process of cleaning the electrode, and the procedure for the deposition of platinum was mentioned earlier[8]. The electrode was activated just prior to use by electrochemical pulsing technique[9]. The sulphuric acid was of 'AnalaR' quality and it was diluted using triply distilled conductivity water. Ethanol was refluxed and distilled thrice and the middle portion was taken. The sulphuric acid solution was pre-electrolysed at a current density of 20 mA cm^{-2} for

* A part of this paper was presented at the Annual Convention of Chemists held in Dec., 1975 at Roorkee.

24 hours in nitrogen atmosphere using platinized platinum foil electrode to remove the impurities (especially organic impurities). Any trace of oxygen present in the test solution was removed by passing purified nitrogen gas. After stopping the flow of nitrogen gas the system was kept undisturbed to attain equilibrium. Then the current-potential readings were noted at steady-state.

In chronopotentiometric single pulse method, the test electrode used was of platinized platinum wire, whose geometric surface area was 0.1 cm^2, and the counter electrode of 2cm^2 platinized platinum foil. The details of the set up were given already[7]. In this sytem a constant current was passed through the test electrode and the auxiliary electrode for a small period using mercury contact switch. The input attenuater of y amplifier of the oscilloscope was set at 0.2V div^{-1} and the time base was varied from 1 sec. div^{-1} to 3 milli sec. div^{-1}. The current density used was varied from 1 mA cm^{-2} to 500 mA cm^{-2}. The oscilloscopic traces were photographed using a camera, from which the transition times were measured[10].

The system was studied at different concentrations of the fuel and the observed values were compared with the hydrogen charging curve. The effect of molybdate ion was studied on the oxidation of ethanol using Galvanostatic as well as Chronopotentiometric methods. For the determination of open circuit potential a freshly anodized electrode was kept in the test solution and the variation of potential with time was noted till a steady value was obtained[11].

All the current density readings were reported on the basis of geometric area and all potentials were referred to the normal hydrogen electrode. Temperature effects were studied using thermostat with an accuracy of ± 0.1°. Unless otherwise specified all the readings were taken using 1*M* sulphuric acid and at temperature 28°.

Results and Discussion

(a) *Kinetic Parameters* : Tafel plots were drawn for the system at different concentrations of the fuel. Fig. 1 was the plot of log. of the concentration of ethanol against log. current density, from which we can conclude that above 1.5 *M* of ethanol the order of reaction with respect to ethanol was zero, whereas below 1.5 *M* the order is one. Increase of temperature was found to decrease the polarization as is shown in the fig. 2. The energy of activation is found from the slope of the plot of log. current density against inverse temperature[12], to be 14 K.cal. $mole^{-1}$ at open circuit potential. *p*H was found to have no effect on the rate. The Tafel slope for the platinized platinum electrode was found to be approximately 120 mV per decade at lower potentials, similar to the observations of Blake et al[4]. This slope was found to be almost constant irrespective of the changes of *p*H, concentration of ethyl alcohol and temperature. At potentials above 0.7V, the slope was found to change rapidly to higher values. The Tafel plot for the oxidation of ethanol at platinized platinum electrode at different concentrations of ethanol and at different temperatures is shown in the Fig. 3. At higher potentials (about 0.8 Volt Vs NHE) formation of the oxide layer over platinum takes place limiting the Tafel region. The oxidation of ethanol through oxides of platinum may be a slow process. Potential oscillations were observed at still higher potentials. The exchange current density was found to be about 10^{-6}A. cm^{-2} which was obtained by extending the curve in the Tafel plot to the reversible potential calculated from thermodynamic data[13]. The effect of molybdate ion as a redox catalyst, and the effect of the oxidation product of ethanol namely acetaldehyde, on the rate of electrochemical oxidation of ethanol is shown in the Fig. 4.

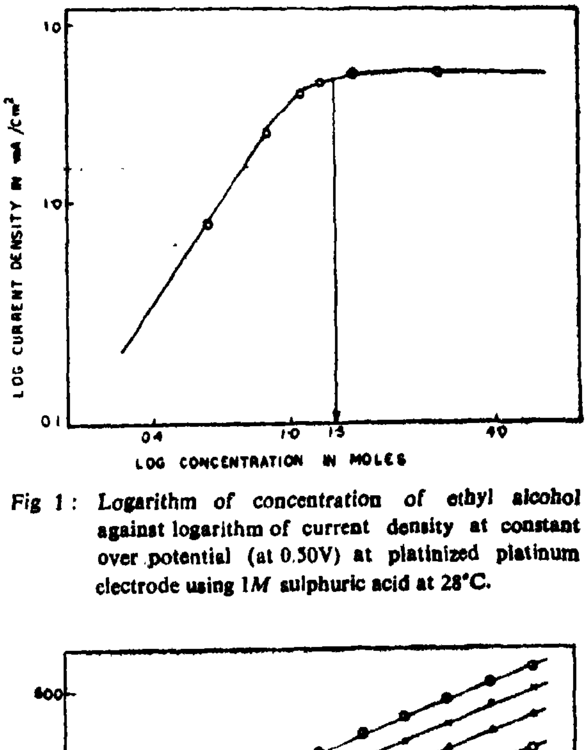


Fig 1 : Logarithm of concentration of ethyl alcohol against logarithm of current density at constant over potential (at 0.50V) at platinized platinum electrode using 1*M* sulphuric acid at 28°C.

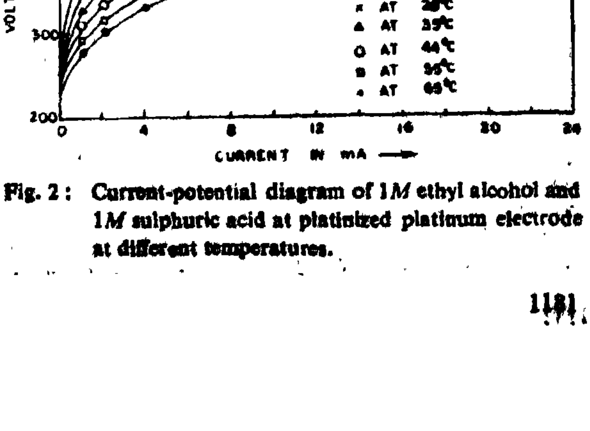


Fig. 2 : Current-potential diagram of 1*M* ethyl alcohol and 1*M* sulphuric acid at platinized platinum electrode at different temperatures.

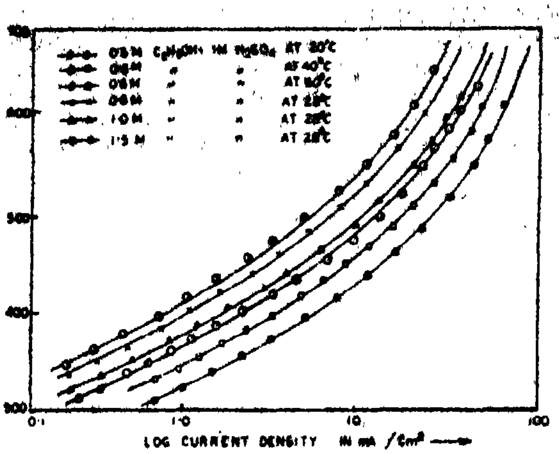


Fig. 3 : Logarithm of current density vs over voltage at platinized platinum electrode in 1*M* sulphuric acid at different concentrations of ethyl alcohol and at different temperatures.

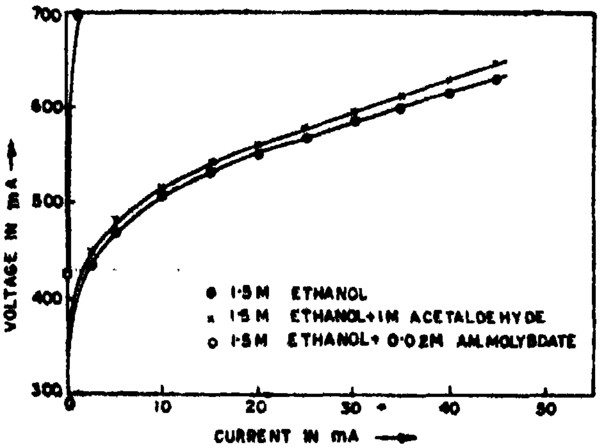


Fig. 4 : Current-potential diagram at platinized platinum electrode in 1*M* sulphuric acid and 1*M* ethyl alcohol, and with the addition of (i) acetaldehyde and (ii) molybdate Mo^{+6} at 28°C.

(b) *Chronopotentiometric Observations* : Chronopotentiometric charging curves were taken in pre-electrolysed sulphuric acid solution, saturated with hydrogen gas. The quantity of charge $i\tau$ required to ionize the monolayer of adsorbed hydrogen was found to be 40 mc cm^{-2}, which was constant for the electrode at different currents. The value of roughness factor about 200, compared to the ordinary value[14] of approximately 1000 may be due to the small amount of platinum deposited. The roughness factor was calculated on the basis of 0.21 mc/cm^2, the charge required for the ionization of monolayer of adsorbed hydrogen[14]. The product $i\tau^{1/2}$ was found to increase continuously with increase of current density, as is given in the Table which indicates that the process is not diffusion controlled[15]. The charging curves in ethanol were taken by keeping the electrode in ethanol-sulphuric acid solution starting from open circuit potential. The quantity of charge required to ionize the adsorbed organic was found to be about 77 mc cm^{-2}. Similar to that of hydrogen charging curves, the product $i\tau^{1/2}$ is not constant, as is given in the table and was increasing continuously as the current was increased. This indicates that the process of oxidation of ethanol is not diffusion controlled and also not controlled by chemical reaction and the process is not accompanied by electro capillary convection. The slope of the graph from the plot of $i\tau^{1/2}$ vs i is positive, which shows that the process is controlled by the oxidation of the adsorbed species[16] which is produced by extremely fast rates of adsorption and desorption of the organic species so that equilibrium is maintained between solution species of the electrode, and the species on the surface[17]. The oxidation of the adsorbed species is not mixed with diffusion according to Laitinen et al[18]. The value of $i\tau$ is constant with in $\pm 7\%$ error in approximation of measuring the transition time.

The transition times observed in the charging curves were started at open circuit potential and limited at approximately 0.75V, above which the formation of oxide layer begins. The potential limit indicates that the oxidation process is ceased above this value when the reaction is inhibited by the oxide layer formed on the electrode surface. This result is in support of Gileadi and Piersma's assumption[2]. The charging curves which were photographed indicate that the double layer charging which is negligible[19] is also included in the oxidation process, as is shown in the Fig. 5.

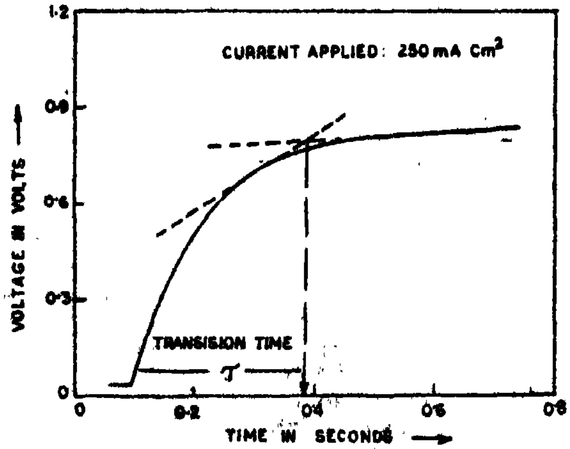


Fig. 5 : Potential-time diagram (chronopotentiometric single pulse) at platinized platinum in 1*M* sulphuric acid and 1*M* ethyl alcohol at 28°C.

It was observed that the charge required to oxidize the adsorbed ethanol on an electrode is almost double to that required for ionization of the adsorbed hydrogen on the same electrode. So it is likely that two electrons are involved in the electro-oxidation of ethanol in the Tafel region. It was observed that the presence of

TABLE SHOWING THE CHRONOPOTENTIOMETRIC DATA

Sl. No.	Chronopotentiometric results of hydrogen gas saturated 1*M* sulphuric acid solution				Chronopotentiometric results of test solution containing 1*M* ethanol and 1*M* sulphuric acid			
	i in mA	τ in sec.	iτ	$i\tau^{1/2}$	i in mA	τ in sec.	iτ	$i\tau^{1/2}$
1.	2.0	20	40	8.94	18	4	72	36
2.	5.5	8	44	15.57	36	2.1	75.6	52.2
3.	12.0	3.3	39.6	21.84	54	1.5	81.0	65.88
4.	20.0	2.0	40.0	28.2	72	1.0	72.0	72.0
5.	30.0	1.2	36.0	33.0	90	0.9	81.0	85.5
6.	40.0	1.0	40.0	40.0	110	0.7	77.0	92.4
7.	50.0	0.8	40.0	45.0	130	0.6	78.0	100.1
8.	100.0	0.4	40.0	63.0	150	0.5	75.0	106.5
9.	150.0	0.27	40.5	78	250	0.3	75.0	137.5
10.	200.0	0.2	40.0	90.0	350	0.24	84.0	171.5

additional acetaldehyde in various concentrations did not change the polarization characteristics of ethanol oxidation. So acetaldehyde was neither adsorbed nor oxidized on the pl tinized platinum electrode in the observed potential range. The fractional surface area covered by the adsorbed species will be approximately 0.8 and this value is similar to that given by Blake et al[4].

(c) *Open Circuit Potentials* : The standard reversible potential calculated from thermodynamic data for ethanol oxidation is $E^{\circ}=0.17V$. Rest potential of the order of 0.20V was observed in IM sulphuric acid solution. These values were found to vary from 0.15V to 0.25V, which may be due to the pre-treatment of the electrode.

From the chronopotentiometric single pulse method it was found that the potential of the electrode in ethanol falls to a minimum after anodic pulse was given and then rises to open circuit potential. This minimum potential corresponds almost to 0.0V, which immediately increases to the open circuit potential of about 0.15V within 1 to 2 seconds. This observed potential minimum, similar to that of formic acid, formaldehyde etc[11,20], was found to be highly dependent on the pre-treatment of the electrode. The minimum in the open circuit potential can be attributed to a mixed potential between hydrogen, resulting from dissociation of ethanol and some organic species[21]. These observations lead to the following scheme for the open circuit decay in ethanol of the platinum electrode being anodized to 1.0V initially

$$\mathrm{Pt\text{-}O + C_2H_5OH \longrightarrow CH_3CHO + H_2O + Pt}$$

$$\mathrm{Pt + C_2H_5\,OH_{soln} \longrightarrow CH_3H_2OH - Pt}$$

$$\mathrm{C_2H_5OH - Pt \longrightarrow CH_3CHOH_{ad} + H_{ad}}$$

$$\mathrm{H_{ad} \longrightarrow H^+ + e}$$

$$\mathrm{C_2H_5OH - Pt \longrightarrow CH_3CHO + 2H^+ + 2e}$$

similar type of reactions for formic acid[11], at platinum electrode were suggested.

(d) *Mechanism of the Reaction* : The observed Tafel slope of about 120 mv per decade indicates that the first electron transfer is the rate determining step. If we write the oxidation of ethanol as

$$(1)\quad \mathrm{C_2H_5OH + Pt \rightleftharpoons C_2H_5OH - Pt}$$

$$(2)\quad \mathrm{C_2H_5OH - Pt \xrightarrow{r.d.s.} C_2H_5O - Pt + H^+ + e}$$

$$(3)\quad \mathrm{C_2H_5O - Pt \longrightarrow CH_3CHO + H^+ + e}$$

considering step 2 as the rate determining step and applying Langmuir type of adsorption, the rate equation can be expressed as

$$v = k\theta_T \exp\left(\frac{\beta VF}{RT}\right)$$

where θ_T is the coverage of the adsorbed species, the other terms having their usual significance. Considering step 1 is in equilibrium as supported by chronopotentiometric results, the above rate expression can be rewritten as, after substituting the value of θ_T from the step 1,

$$v = k'\, C_{C_2H_5OH} (1-\theta_T) \exp\left(\frac{\beta VF}{RT}\right)$$

The rate equation satisfies the observed Tafel slope, first order reaction with respect to ethanol and the independence of rate with pH of the solution.

The rate equation indicates that the order of the reaction with respect to ethanol is one. But according to the observed values it was found that at higher concentrations of ethanol the order was tending to zero. The first order reaction with respect to ethanol was found up to the concentration of approximately $0.3M$ by Liang et al.[3], and $0.5M$ by Sunderland et al[4], on bright platinum and in the present investigation about $1.5M$ on the platinized platinum. This increase in the limiting concentration of ethanol compared to the previous values may be due to the increase of surface area of platinized platinum compared to the bright platinum.

Assuming the fraction of the electrode surface covered by the species other than ethanol, like CH_{3ad}, CH_2OH_{ad}, $CHOH_{ad}$, etc[6] remaining constant and low and considering θ_T, which is almost equal to C_2H_5OH–Pt, reaching to limiting value as the concentration of the ethanol increased to $1.5M$, the rate expression becomes independent of the concentration of ethanol.

It was known that at potentials higher than 0.8V, the formation of oxide layer begins on the electrode[2,9], which can be expressed as

(4) $Pt + (H_2O)_n \longrightarrow Pt-(OH)_n + nH^+ + ne$

(5) $Pt-(OH)_n \longrightarrow PtO_n + nH^+ + ne$

At these potentials the oxide layer formation begins also from the adsorbed ethanol species as suggested[1],

(6) $Pt + n\,EtOH \xrightarrow{\text{slow}} Pt\,(OEt)_n + nH^+ + ne$

(7) $Pt(OEt)_n + nH_2O \longrightarrow Pt(O)_n + n\,CH_3CH_2OH + nH^+ + ne$

so, as the potential is increased from open circuit to about 0.70V the reaction steps 1, 2 and 3 will occur. But as the potential is increased to still higher values, oxide layer formation occurs through steps 4 to 7 decreasing the available sites for ethanol to adsorb. This type of blocking of surface by the oxide layer decreases the value of θ_T to low value, which on the other hand decreases rate of oxidation. The occurence of this type of multistep reactions at higher potentials may be causing a change in the Tafel slope from 120 mv to higher values.

The potential oscillations which were observed at still higher potential might be considered due to the formation of oxide layer on the electrode by electrochemical process as indicated and simultaneous chemical reduction of the so formed oxide layer by ethyl alcohol. At higher potentials electrochemical process predominates the chemical process, thereby making the oxide layer formation irreversible. This makes the electrode inactive for the oxidation to occur.

(e) *The Effect of Molybdate Ion on the Rate*: In the presence of molybdate ion in ethanol-sulphuric acid solution the product $i\tau^{1/2}$ was found to be constant and independent of current. The $i\tau^{1/2}$ was found to be dependent on the concentration of molybdate ion and was increasing proportionally with increasing concentration of molybdate ion. This indicates that the process was controlled by the diffusion of that ion[15]. The polarization in the oxidation of ethanol in presence of molybdate ion was found to be considerably high as is shown in the Fig. 4. So it appears that the chemical reaction[16]

$$CH_3CH_2OH + Mo^{+6} \longrightarrow CH_3CHOH + Mo^{+5} + H^+$$

is the slow step in the electrochemical oxidation of the ethanol at platinized platinum electrode in presence of molybdate ion. Mo^{+5} being subsequently oxidized to Mo^{+6} at the electrode.

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Notes

Radiation Protective Agents : Synthesis of Some N'-substituted mercapto alkyl guanidines, Isothiouronium salts and Thiosulphuric acid derivatives I.

P. G. AGNIHOTRI and J. P. TRIVEDI*

M. G. Science Institute, Ahmedabad 380 009

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AMINOTHIOLS exhibit very remarkable radiation protective property. Patt[1] in 1949 discovered the radiation protective property of cysteine in mice. In 1951, Bacq et al[2] reported the effectiveness of cysteamine(MEA) and cystamine—the decarboxylation products of cysteine and cystine respectively. 3-Mercaptopropylamine (MPA) and 4-mercaptobutylamine (MBA) have also been shown to possess anti-radiation property[3]. Doherty et al[4] introduced aminoethyl isothiouronium bromide hydrobromide (AET) in 1955, pointing out its superiority to other thiols, particularly in respect of its effectiveness after oral administration, the simplicity of synthesis and its stability on storage. This compound rearranges *in vivo* to 2-mercaptoethyl guanidine (MEG) which seems to be responsible for its radiation protective property. Various N'-Alkyl derivatives of MEG have been synthesised and tested by Shapira et al[5]. When the thiol group in the aminothiols is replaced by a thiosulphate group, Bunte salts are obtained which equalled the parent compound in their protective activity, but such compounds are much less toxic. For example, 5-2-aminoethyl-thiosulphuric acid is a well-known radioprotector[6].

In the present communication, synthesis of some N-Aryl-N'-(ω-mercapto) alkyl guanidines, their corresponding isothiouronium salts and thiosulphuric acid derivatives have been described. The aromatic guanidines prepared from substituted anilires with the help of S-Methyl isothiourea sulphate, were treated with excess of α-W-dibromo alkanes in presence of pyridine to yield N-Aryl-N'-(ω-bromo) alkyl guanidines(I) These with sodium hydrogen sulphide and thiourea afforded N-Aryl-N'-(ω-mercapto)alkyl guanidines(II) and isothiouronium salts (IV) respectively. The thiosulphuric acids(III) were obtained by treating the hydrobromide salts of bromoalkylguanidines (I) with sodium thiosulphate. (Figure 1).

$$R\text{-}C_6H_4\text{-}NH\text{-}C(=NH)\text{-}NH[\ H_2]n^{x}$$

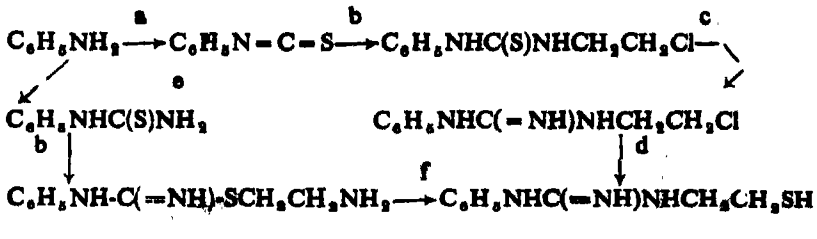
I X=Br   II X=SH   III X=S.SO$_3$H

IV X = -S-C(=NH)NH$_2$.HBr

R=H, 4-CH$_3$, 4-OCH$_3$, 4-OH, 4-Cl, 4-Br, 4-N(CH$_3$)$_2$, 4-NHCOCH$_3$

Fig. 1.

Experimental proof for the structure of N-Aryl-N'-(ω-mercapto)alkyl guanidines ('I) was provided by two other routes depicted in Figure 2.



a. CS$_2$, NaOH   b. H$_2$NCH$_2$CH$_2$Cl   c. PbO, NH$_3$(desulphurization)[7]

d. NaSH   e. NH$_3$ f. NaOH(transguanylation)[8].

Fig. 2.

* Present address : R & D Department, Cadila Laboratories, Ahmedabad-380 008.

Experimental

Preparation of N-arylguanidines: The mixture of S-methylisothiourea sulphate (0.3 mole) and pure amine (0.6 mole) was heated to a temperature of 150° – 170° by means of an oil bath. In some cases, where water was used as a solvent, the mixture was refluxed. Methyl mercaptan evolved was absorbed in 20% solution of NaOH. The heating was continued until there was no further evolution of methyl mercaptan. The solid mass obtained was intimately incorporated with 95% ethanol and allowed to stand for 24 hours. The solid guanidine sulphate containing some amine sulphate was filtered off, washed with little cold water and dried. Purification was done by converting sulphate into carbonate using $Ba(OH)_2$ and CO_2. The yield was about 55-60% of the theoretical.

TABLE 1 : $R-C_6H_4-NH-C(=NH)\,NH(CH_2)nX$

R	n	m.p.(I)* [X=Br]	m.p. (II)** [X=SH]	m.p.(III)** [X=S.SO$_3$H]	m.p. (IV)** [X=SC(=NH)NH$_2$.HBr]
H	2	118	126	105	116
H	3	119	123	103	107
H	4	121	128	97	104
4-CH$_3$	2	155	143	207	128
,,	3	147-148	144	183	129
,,	4	151-53	141	219	142
4-OCH$_3$	2	148	140	211	150
,,	3	152	144	214	137
,,	4	143	118	209	132
4-OH	2	212-15(d)	173	236(d)	154
,,	3	219	164	310(d)	69
,,	4	325	151-52	295(d)	81-82
4-Cl	2	140	127	202	125
,,	3	137	136	288	117
,,	4	136	141	177	124
4-Br	2	132	129	177	107
,,	3	140	131	304(d)	126
,,	4	122	129	195(d)	121
4-N(CH$_3$)$_2$	2	130	99	119	95
,,	3	129	118	117	64
,,	4	127	126	156	101
4-NHCOCH$_3$	2	137-38	179	298(d)	189
,,	3	294-(d)	158-60	314(d)	140
,,	4	142-43	149	294	190

*N and Br. analysed and found to be within experimental limits.
**N and S ,, ,, ,,

Preparation of N-aryl, N'(ω-bromo)alkyl guanidines : I. The appropriate guanidine sulphate (0.1 mole) α,ω-dibromoalkane (0.2 mole) and pyridine (0.15 mole) were refluxed by means of an oilbath for a period of about 3 to 4 hours. The mixture was then poured in ice-cold water. The aqueous layer was separated and washed with ether. It was then neutralized by adding sodium bicarbonate. Free base was separated as precipitates upon vigorous scratching. It was then filtered, washed with water, dried and crystallized from ethanol. The yield was in the range of 55-70% of the theoretical amount.

Preparation of N-aryl, N'(ω-mercapto)alkyl guanidine : II. N-aryl-N'(ω-bromo)alkyl guanidine (0.01 mole) and sodium hydrogen sulphide (0.01 mole) were dissolved in ethanol and the mixture was refluxed for about half an hour on water-bath. Sodium bromide separated on cooling, was filtered off and the filtrate on standing gave the crystals of the mercapto compound. It was filtered, dried and recrystallized from rectified spirit. The yield was about 70% of the theoretical amount.

Preparation of N-aryl, N'(ω-thiosulphuro) alkyl guanidines (Bunte Salts) : III. The hydrobromide salt of N-aryl, N'(ω-bromo)alkyl guanidine (0.01 mole) and sodium thiosulphate crystals (0.01 mole) were dissolved in slightly more than the required amount of warm water, then refluxed for about half an hour and filtered. The crystals of the Bunte salt were obtained on cooling. The yield was about 80-90% of the theoretical amount.

Preparation of Isothiuronium salts : IV. Equimolar amounts of N-aryl, N'(ω-bromo)alkyl guanidine and thiourea were dissolved in ethanol and the mixture was refluxed for about 15 minutes on water-bath. The solution was then concentrated to half of its volume, cooled and diluted with equal volume of ethyl acetate. The mixture was then chilled, stirred and scratched to give the crystals of isothiuronium salt.

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Palladium(II) Complexes of α-Oximino-acetoacetarylamide Benzoylhydrazones

M.M. PATEL*, M.R. PATEL & B.N. MANKAD

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat

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In continuation of our previous work on synthesis of α-oximino-β-hydrazinoacetoacetarylamides[1], their analytical aspects[2-4] and Pd(II) complexes[5], the present paper deals with the preparation and characterisation of Pd(II) complexes with α-oximinoacetoacetarylamide benzoylhydrazones.

Experimental

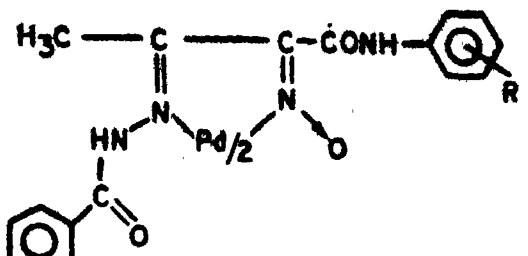
Preparation of the complexes : 10 ml. aq. solution of Pd(II) chloride (0.05 *M*) was gradually added to 25 ml alcoholic solution (2%) of α-oximinoacetoacet-*o*-chloroanilide benzoylhydrazone and acidified with dil. HCl. The mixture was diluted to about 100 ml with distilled water and digested on waterbath for half an hour ; the bright yellow precipitates obtained were filtered, washed with hot water and aq, ethanol (1:1), and dried in an oven at 110°.

The Pd(II) complexes of the other α-oximinoacetoacetarylamide benzoylhydrazones of the series were prepared in the same manner, The m.p., colour, elemental analysis and composition of the complexes are given in Table-1. The infrared spectra of the ligands and complexes and the electronic spectra of the ligands in ethanol solution were recorded.

Results and Discussion

Electronic spectra of the ligands : The chromophoric system N=C–C–C=O (with =N on the middle carbon) in the ligands exhibits two bands, one at 230-35 nm (C = 18500-27400) and second at 275-79 nm (C=16500-20300). Comparison of these spectra with those of acetoacetarylamide benzoylhydrazones with chromophoric system, N=C-CH_2-C=O (Band I, 250-258 nm, C=15100 to 26400, Band II, 229-230 nm, C = 16100 to 17200)[6] reveals that there is hypsochromic effect (△C = 1800-3900) in Band I and there is a bathochromic displacement of the Band II to the extent of 46-50 nm, without appreciable change in intensity.

TABLE 1—PALLADIUM COMPLEXES OF α-OXIMINOACETOACETARYLAMIDE BENZOYLHYDRAZONES



No.	R	Composition	Colour	m p. °C (decomp.)	% Palladium Found	% Palladium Reqd.	% Nitrogen Found	% Nitrogen Reqd.
1	*p*-CH_3	$C_{36}H_{34}O_8N_8Pd$	Golden yellow	360	13.74	13.67	14.30	14.35
2	*o*-Cl	$C_{34}H_{28}O_6N_8Cl_2Pd$	Bright ,,	320	12·44	12.98	13.80	13.63
3	*p*-Cl	$C_{34}H_{28}O_6N_8Cl_2Pd$	,, ,,	325	12.83	12.98	13.63	13.79
4	*o*-OCH_3	$C_{36}H_{34}O_8N_8Pd$	Golden ,,	300	13.30	13.12	13.85	13.78
5	*p*-OCH_3	$C_{36}H_{34}O_8N_8Pd$	Orange	327	13.16	13.12	13.72	13.78
6	*m*-2,4-$(CH_3)_2$	$C_{38}H_{38}O_6N_8Pd$	Golden yellow	330	13.31	13.19	13.91	13.85
7	*m*-Cl	$C_{34}H_{28}O_6N_8Cl_2Pd$	Bright ,,	305	12.92	12.98	13.78	13.63
8	*p*-OC_2H_5	$C_{38}H_{38}O_8N_8Pd$	Orange red	320	12.55	12.69	13.27	13.32

Infrared spectra: The important infrared spectral bands and their assignments are based on the study of the free ligands and their Pd(II) complexes. The strong band at 3480-3500 cm^{-1} appears in the ligands but does not appear in the corresponding complexes. This suggests the presence of intramolecular hydrogen bond in the ligands. This band is within the expected region for intramolecular hydrogen bonding[7]. The absence of such band in the complexes is the indication of the replacement of hydrogen of oximino group by metal ion. The strong band at 990-1005 cm^{-1} in the ligands is attributed to N-O stretch. In the complexes this band shifts to 1170-1180 cm^{-1}. The N-O stretches of nitrogen and oxygen coordinated oximino groups are expected to shift to higher and lower frequencies respectively compared to that of the ligands. The increase in N-O frequency shows the coordination through nitrogen of oximino group. This further agrees with the usual behaviour of oximino group to coordinate through nitrogen atom[8-11]. According to Sterk and Ziegler (C=N, 1625 cm^{-1})[12], the strong band around 1590 1615 cm^{-1} in the ligands indicates C=N stretching frequency. In the complexes this band appears around 1570-1600 cm^{-1}. The lowering of the C=N stretching frequency is an indication of the coordination of 1-nitrogen of benzoyl hydrazide. The infrared spectra of the ligands and complexes reveal bands of strong, medium or weak intensity around 3300, 3070 and 3440 cm^{-1} indicating secondary trans association and free N-H vibrations of amides respectively[13].

From the spectra it is evident that ligands as well as complexes in the solid state are mostly in the associated form. The probable associations are due to hydrogen bonding between carbonyl groups and hydrogen of the amide and benzoylhydrazide moieties. The strong band around 3300 cm^{-1} is considered to be due to trans associated form. The strong bands in the ligands and complexes around 1655 and 1680 cm^{-1}, 1550 and 1530 cm^{-1} and 1300 and 1260 cm^{-1} are attributed to amide I, amide II and amide III bands, as associated and free forms respectively[13].

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Kinetics and Mechanism of Hydrolysis of Sec. Amyl Bromide in Neutral Medium

VIJAI SWAROOP and DHARAM PRAKASH*

Chemical Laboratories, Directorate of Geology and Mining, (U.P.), 2-Way Road, (27/4, Ram Mohan Rai Marg), Lucknow (U.P.), India.

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FEW compounds,[1,3,4,5,6,7] in the alkyl halide series, have been investigated to show the olefin elimination kinetically independent of simultaneous substitution in alkaline medium, but the literature regarding the studies to show the kinetic dependence of olefin elimination and substitution processes which occur simultaneously in the solvolysis of halides is scanty. The present investigation mainly deals with the kinetic dependence of both processes which simultaneously occur in neutral hydrolysis of sec-amyl bromide. Olefin elimination and simultaneous substitution reactions both followed first order with respect to the halide. Total first order rate constant has been split up into its constituents (Olefin elimination and substitution rate constant) by suitable measurement of olefin formed. The present investigation also includes the effect of change in the composition of the medium on the rate of reactions, calculation of separate energies of activation in both processes, effect of salt on rate of reaction. In the present case, the unimolecular processes may take place through the scheme given by Moelwyn-Hughes and Fells[8].

Experimental

Sec-amyl bromide was dried over anhydrous sodium carbonate and calcium chloride and then fractionated. The fraction collected at 11 °-118° (B.P.) was used for all measurements.

The value of first order rate constant was determined by estimating the acid produced as a result of hydrolysis of halide at various intervals of time and by employing the usual integrated formula for first order. The olefin was estimated by the following method. The sealed ampule containing 5 ml. of the reaction mixture was first cooled and then broken by shaking under water at 0° in an evacuated stoppered flask provided with an inlet and outlet tube, the former reaching the bottom. The flask was kept at 50°-60° in a water bath and the whole amount of olefin produced was swept by passing a slow stream of nitrogen and bubbling the gas in a flask containing a known amount of bromine in carbon tetra chloride. The remaining bromine was estimated by titrating it against standard thiosulphate. The substitution product was indentified as sec-amyl alcohol by the method described earlier.[3,4,5,6,7,10].

Results and Discussions

Experimental results are presented in Tables 1-2. Table 1 records the total first order rate constant

TABLE 1

k'_1 in min.$^{-1}$ Limits of accuracy are ±2.7% or less.

Temperature (°C)	[EtOH – H_2O] (V/V %)	[KBr]× M	$k'_1 \times 10^5$
[Sec – amyl bromide] = 7.97×10^{-2} M			
55	80	—	1.82
,,	75	—	4.84[a]
,,	70	—	7.60
,,	65	—	9.11[a]
,,	60	—	23.85
,,	55	—	95.02
,,	50	—	143.66[a]
,,	45	—	201.44
,,	40	—	262.61
,,	60	0.25	23.00
,,	,,	0.50	21.85[b]
,,	,,	0.75	20.62[b]
,,	,,	1.00	19.24
,,	,,	1.25	17.92
,,	,,	1.50	15.67[b]
40	,,	—	4.37[c]
45	,,	—	8.12[c]
50	,,	—	12.74
60	,,	—	38.56[d]
65	,,	—	64.60[c]
70	,,	—	107.72[d]
75	,,	—	170.18[d]

a: ±2.5%, *b*: ±1.2%, *c*: ±2.8%, *d*: ±3.6%.

* For correspondence.

TABLE 2

[Sec – amyl bromide] = 7.97 × 10^{-2} M

[EtOH – H_2O] = 60% V/V

Experiment	Temperature (°C)	E_1 (%)	SN_1 (%)	$\frac{Sn_1}{SN_1+E_1}$	$\frac{E_1}{SN_1+E_1}$	$k'_1 \times 10^6$ min^{-1}	$k'_1S \times 10^6$ min^{-1}	$k'_1E \times 10^6$ min^{-1}
1	75	5.90	94.10	0.9410	0.0590	170.18	160.14	10.04
2	70	5.73	94.27	0.9427	0.0573	107.72	101.55	6.17
3	65	5.55	94.45	0.9445	0.0555	64.60	61.01	3.59
4	60	5.41	94.59	0.9459	0.0541	38.56	36.47	2.09

obtained under various physical conditions, mentioned in colums 1,2 and 3. The increase in the velocity of first order process on addition of water to the reaction mixture is in accordance with the findings of Bliel et al[8] and the theory of solvent action[9]. The decrease in the first order rate constant by an initial addition of potassium bromide may be attributed to the decrease in the nucleophilic activity of water molecules associated with the increase of ionic strength of the medium.

The percentage of olefin obtained in the unimolecular process (shown in column 3 of table 2) are the average of at least three observations. E_1 and SN_1 terms stand for the reactions occurring through unimolecular elimination and unimolecular substitution processes. The fractions contained in columns 5 and 6 were averages of observations taken at various intervals of time and they were almost constant which shows that these fractions actually represent the ratios in which the total unimolecular process has been rightly split up into unimolecular substitution and elimination processes. These factors of columns 5 and 6 of table 2 will give the rate constants for unimolecular substitution and elimination respectively (columns 8 and 9) on multiplication with total unimolecular rate constant (column 7). A perusal of table 2 shows that unimolecular substitution is faster than unimolecular elimination which may be attributed to predominance of inductive effect (responsible for former) over electrometric effect (responsible for latter).

The values of energy of activation for unimolecular substitution, unimolecular elimination and total unimolecular reaction come out to be 23.12, 24.59 and 22.06 kcal/mole respectively. The corresponding values of entropy of activation for above reactions have been worked out to be −15.19, −16.44 and −18.28 e.u. respectively.

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Phosphate Release from Basic Slags by EDTA

D. N. PATHAK

Department of Chemistry,
Regional Institute of Technology,
Jamshedpur.

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WALLACE and coworkers[5] studied the use of metal chelates as a source of micronutrient supply to plants. Das[1] in a recent publication suggested the possibility of using zinc-EDTA as a combined micronutrient fertilizer and soil iron mobilizer. Of late Hajra and Chakravarti[4] advocated the use of some chelating agents to release phosphate from minerals.

TABLE 1—ANALYSIS OF BASIC SLAGS

Ingredients.	TBS	BBS	DBS	MBS	KBS	RBS
SiO_2	14.60	15.95	27.16	20.51	25.02	33.12
FeO	28.00	10.30	5.54	9.32	10.21	0.58
MnO	3.20	4.68	5.00	9.14	10.47	2.52
CaO	32.73	41.72	36.65	43.49	39.39	33.33
MgO	6.23	6.38	6.28	9.45	11.46	6.23
Al_2O_3	6.44	7.39	16.01	5.63	1.62	23.12
P_2O_5	7.84	3.58	3.21	1.49	0.88	0.26
Trace elements	Zn, Cu, Mo, Co, Cr, Ni, Sn, Ti, V	Zn, Cu, Mo, Cr, Ni, Ti, V	Zn, Cu, Mo, Co, Ti, V	Zn, Cu, Mo, Co, Cr, Ni, Sn, Ti, V	Mo, Ni, Cr, Ti, V	Mo, Cr, Ni, Co, Ti, V

TABLE 2—RELEASE OF PHOSPHATE FROM BASIC SLAGS

Slag (1 g)	Initial values without EDTA		FILTRATE: Initial values		After 24 hours		After 3 days		After 7 days	
	*p*H	P_2O_5 %	*p*H	P_2O_5 %	*p*H	P_2O_5 %	*p*H	P_2O_5 %	*p*H	P_2O_5 %
TBS	8.05	0.0005	6.05	3.3985	6.95	3.3991	7.75	3.4005	8.00	3.4032
BBS	9.00	0.0002	7.05	1.2802	8.00	1.2804	8.80	1.2810	9.00	1.2820
DBS	8.95	0.0002	6.95	1.2505	7.85	1.2507	8.65	1.2512	8.90	1.2523
MBS	10.60	0.0001	8.65	0.4800	9.60	0.4820	10.45	0.4804	10.55	0.4809
KBS	9.10	traces	7.15	0.3798	8.05	0.3799	8.90	0.3800	9.05	0.3803
RBS	7.60	traces	5.60	0.1200	6.50	0.1202	7.30	0.1202	7.55	0.1203

TBS = Tatanagar Basic Slag
BBS = Burnpur Basic Slag
DBS = Durgapur Basic Slag
MBS = Madhya Pradesh (Bhilai) Basic Slag
KBS = Karnatak (Bhadrabati) Basic Slag
RBS = Rourkela Basic Slag

The application of basic slags for increasing crop production has been suggested by several workers. To mention some recent advances on the subject are those of Mandal and Jha[8] whose extensive researches have demonstrated the suitability of Indian basic slags for neutralizing acid soils, an essential condition for increased crop productivity. The analysis shows that the slags contain a number of micronutrient elements and phosphate besides calcium and magnesium. The present investigation is therefore designed to find out the possibility of utilizing EDTA to release phosphate from Indian basic slags.

Experimental

Basic slags from six different steel mills of India namely Burnpur, Durgapur, Tatanagar, Rourkela, Madhya Pradesh (Bhilai) and Karnatak (Bhadrabati) were powdered and sieved through a 100 mesh sieve. The samples passing through the sieve were analysed and used in the subsequent experiments. 1 g each of different basic slags was taken in stoppered glass bottles and thoroughly treated with 100 ml distilled water. The initial *p*H values of the systems were recorded. Each of these samples were then thoroughly treated with 0.1 g EDTA and immediately *p*H values were noted. One drop of chloroform was added to each bottle with a view to suppress fungus growth.

The samples with above treatments were stirred thoroughly and incubated separately for three different lengths of time, such as 24 hours 3 days and 7 days. After the desired period of incubation the solutions were filtered and *p*H and P_2O_5 of the filtrates were determined. To determine P_2O_5 the filtrates were digested with a mixture of conc. H_2SO_4 and HNO_3 to break the complexed metal ions and to decompose the organic

substances. These were evaporated to dryness, brought back into solutions by adding in each case 5 ml conc. HCl, 20 ml conc. HNO_3 and 50 ml water. The solutions were again digested with 10 g NH_4NO_3 at 90° for about 10 minutes. The digested solutions were diluted and the amount of P_2O_5 in each case was estimated volumetrically after precipitating with ammonium molybdate solution[4].

Discussion

The analysis (Table 1) shows that all the Indian basic slags contain some micronutrient elements besides calcium, magnesium and phosphorus and is suitable for healthy plant growth. The results (Table 2) indicate that the release of phosphate from basic slags by water is very little and when EDTA is used the release increases to a marked extent.

As metal chelates may be directly used as source of micronutrient supply to plants[5], it can be concluded from this investigation that a mixture of EDTA and basic slag is very useful for supplying micronutrient elements and phosphorus to plants.

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Effective Rigid Molar Volume of Salts in Dioxane-Water Mixtures from Viscosity Data

P. B. DAS

Department of Chemistry, S. C. S. College, Puri.

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THE properties of aqueous electrolytic solutions are highly specific to individual ions concerned and *generalisations are difficult to find. In case of* viscosity, Jones-Dole[1] developed an empirical equation for the concentration dependence of viscosity of dilute electrolytic solutions, given by,

$$n_r = 1 + A\sqrt{C} + BC \qquad (1)$$

where n_r is the relative viscosity, C is the concentration (moles/litre) and A and B are constants specific for the given solute-solvent system. This well known equation has undergone extensive investigation. Although the 'B' coefficient is empirically derived, it is a highly specific property of the solute and can be determined by adding the individual contributions of the solute constituent ions. Thus,

$$B = z_+B_+ + z_-B_- \qquad (2)$$

Fuoss and coworkers[2,3] working with apparent molar volume (V), obtained from the density measurements, were successful in domonstrating a like correspondence between additivity of ionic contributions to both B and V. However they were not able to confirm the Einstein[4] equation :

$$B = 2.5\ V \qquad (3)$$

where 'V' is an estimation of molar volume of the solute molecules in solutions and found it valid only for large ions which can be said to resemble macroscopic particles. However, Kuruscev et al[5], reported that the equation (3) is only valid for ions of radius 5A°. Breslau and Miller[6] designate this 'V' as the effective rigid molar volume 'V_e' and can be calculated as :

$$V_e = \frac{-2.5C + [(2.5C)^2 - 4(10.05\ C^2)(1-)n_r]^{\frac{1}{2}}}{2(10.05)C^2} \qquad (4)$$

If the viscosity concentration data are available *for* any given salt, V_e may be obtained by the above equation and the average value is obtained. The V_e thus calculated is a fictitious or effective volume i. e. it is that volume which a mole *of* solute particles behave like when considered, from purely hydrodynamic reasons, as rigid macroscopic spheres. A particle which has a measure effect on neighbouring solvent molecules, *from physical considerations alone*, would be expected to have a higher V_e than one which has a lesser effect. Since the 'B' coefficient is an empirical measure of the ion-solvent interaction, a relation should therefore exist, *with a positive slope, when 'B' is plotted against 'V'*. From the plot the following correlations have been obtained:

$$\text{Monovalent} - B = 2.90\ V_e - 0.018 \qquad (5)$$

$$\text{Bivalent} - \quad B = 6.06\ V_e - 0.041 \qquad (6)$$

This has been extended to mixed solvents, namely *dioxane-water* mixtures and an attempt has been made to find the correlation of the 'B' coefficient with V_e for seventeen salts at 10, 20 and 30% dioxane-water mixtures i.e. by changing the dielectric constants. The 'B' coefficient have been taken from our own data[7-10]. The average V_e have been calculated by means of equation (4) and have been tabulated in table 1 along with the 'B' values. The plot of 'B' against V_e is found to be linear and the following equations are satisfied.

$$10\%\ \text{Dioxane} - B = 1.33V_e - 0.020 \qquad (7)$$

$$20\%\ \text{Dioxane} - B = 2.19V_e - 0.035 \qquad (8)$$

$$30\%\ \text{Dioxane} - B = 3.25V_e - 0.100 \qquad (9)$$

This indicates that the slope of the plot of 'B' vs V_e changes with the change in the dielectric constant and this slope is found to be linear with 'D'. This change can be explained as follows: as a result of solute-solvent interaction, small density changes take place at the interface between the solute and solvent molecule. This density changes lead to changes in the microscopic viscosities of the solvent at the interface and thus, appear as increases or decreases in the Einstien's slope, depending on whether the microscopic viscosities is, respectively, higher or lower than the pure solvent value. As the 'D' changes i.e. decreases the divalent ions, as a result of their higher charge density, tend to induce much more structuring in the solvent at the interface and thus the microscopic viscosities of the solvent at the interface is higher than that it would be at high 'D'.

TABLE 1

Salts	10%D B	10%D V_e	20%D B	20%D V_e	30%D B	30%D V_e
$BaCl_2$	0.230	0.112	0.405	0.162	0.648	0.243
$BaBr_2$	0.284	0.130	0.440	0.197	0.648	0.286
$Ba(NO_3)_2$	0.110	0.064	0.280	0.122	0.330	0.153
$Ba(ClO_4)_2$	0.267	0.128	0.390	0.150	0.600	0.226
$MgCl_2$	0.430	0.190	0.540	0.244	0.640	0.292
$MgBr_2$	0.460	0.191	0.600	0.247	0.870	0.358
$Mg(NO_3)_2$	0.380	0.161	0.420	0.195	0.500	0.216
$Mg(ClO_4)$	0.380	0.122	0.480	0.214	0.770	0.270
$CaCl_2$	0.330	0.128	0.400	0.164	0.460	0.201
$Ca(NO_3)$	0.340	0.130	0.390	0.156	0.433	0.194
$SrCl_2$	0.350	0.138	0.500	0.194	0.620	0.199
$Sr(NO_3)_2$	0.200	0.107	0.270	0.118	0.400	0.147
K_2SO_4	0.280	0.122	0.300	0.138	—	—
Na_2SO_4	0.300	0.130	0.325	0.148	0.410	0.146
$MgSO_4$	0.690	0.278	0.700	0.289	—	—
$ZnSO_4$	0.760	0.292	0.810	0.397	—	—
$NiSO_4$	0.700	0.269	0.790	0.287	—	—

A gradual increase in viscosity and hence an increase in 'B' value is observed as the dioxane is increased (Table 1). This phenomenon is obvious in terms of increasing molecular association[11] between water and dioxane with the formation of bigger molecules.

The values of 'V_e' also increases with the increase in dioxane content of the solvent. This is in complete analogy with the theoretical expression. This may be interpreted in terms of hydrogen bond formation between water and dioxane molecules. As dioxane is increased more and more hydrogen bonded dioxane-water molecules are formed resulting in increase in the value of V_e (table 1).

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Proximate and Amino Acid Composition of Some Hybrid Varieties of Rice

J. D. CHAVAN and N. G. MAGAR*

Department of Analytical Chemistry and Biochemistry, Institute of Science, Bombay-400 032.

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RICE, a vital commodity and principal food crop providing a large portion of human sustenance to about half the world population, is a staple food in India and other Asian countries. To feed the expanding population is a tremendous task and therefore rice breeders are anxious to evolve high yielding varieties of rice to meet this challenge. It has been observed that the composition of rice varies with variety, plant-type, soil conditions, maturing, location, soil moisture and weather conditions prevalent at the time of grain filling.[1] It was therefore thought necessary to study the chemical composition of recently evolved high yielding varieties of rice grown in the State of Maharashtra.

* Present address: Department of Biochemistry, G. S. Medical College, Parel, Bombay-400 012.

Material and Methods : Eleven hybrid varieties of rice obtained from the Rice Specialist, Konkan Krishi Vidyapeeth, Karjat, Kolaba District, Maharashtra were chosen for the present investigation. The varieties were (1) Jaya, (2) Satya, (3) Soorya, (4) Suhasini, (5) IR8, (6) TN_1, (7) K-14-7, (8) K-7-3A, (9) K-184, (10) P-60 and (11) R-68-1-1. All these varieties were dehusked by hand pounding and the brown rice so obtained was floured and the flour used for analysis.

Protein, ash, fat and crude fiber contents were determined by AOAC[2] methods. Total carbohydrate and reducing sugars were estimated by Cole's ferricyanide method.[3] Available lysine was estimated by Carpenter's method[4] and amino acid composition by paper chromatography method.[5]

Results and Discussion

Table 1 represents the proximate and available lysine composition of these varieties. Protein content varied from 6.16 to 8.10% being highest for Satya and lowest for P-60. Raghavaiah and Kaul[6] analysed Basmati and TN_1 for protein content and found as 8% and 12.1% respectively. Raghavaiah et al[1] did so for Basmati, Jaya and IR8 and reported the same as 10.5%, 8%, 8% respectively. Protein content reported by Mitra and Das[7] for IR8 and TN_1 was 10.06% and 13.21% respectively. The protein content of Jaya, IR8 and TN_1 in this investigation was 7.7%, 7.9% and 7.4%. It is evident from these observations that the same variety differs in its protein content. This may be due to region, cultivation, growth conditions, fertilisers, soil and other factors.

Amino acid composition is presented in Table 2. FAO[8] reference pattern of amino acid requirements and Eggum[9] amino gram for rice have been given for comparison. It is clear from these results that all the essential amino acids are present in these varieties. Available lysine (Table 1) was found to be about 60 to 70% of total lysine. Among these varieties Satya and Soorya had a very high content of available lysine. Essential Amino Acid Index[10] (E.A.A.I.), Biological Value[11] (B. V.) and Chemical Score[12] were calculated from the essential amino acid composition of these varieties and presented in Table 3. E.A.A.I. varied from 68.42 to 85.53 being highest for R-68-1-1 and lowest for TN_1. The B V. ranged between 62.88 and 81.52 and was highest for R-68-1-1 and lowest for TN_1. The chemical score varied from 50.01 to 64.28 being highest for R-68-1-1 and lowest for P-60. It is clear from the above discussion that R-68-1-1 variety is biologically superior to all other varieties on the basis of E.A.A.I., B. V. and Chemical Score.

TABLE 1—PROXIMATE COMPOSITION AND AVAILABLE LYSINE CONTENT OF RICE

(on wet basis)

No.	Variety	Protein %	Fat %	Ash %	Total Carbohydrate %	Crude fiber %	Reducing sugar %	Available lysine*
1.	Jaya	7.70	1.50	0.98	79.55	0.80	0.42	2.41
2.	Satya	8.10	1.60	1.06	79.54	0.90	0.37	3.02
3.	Soorya	7.50	1.35	1.00	79.64	0.95	0.34	2.80
4.	Suhasini	6.90	1.45	1.02	76.78	0.80	0.41	3.04
5.	IR8	7.90	1.20	1.02	79.50	0.87	0.36	1.68
6.	TN_1	7.40	1.35	1.09	76.70	0.81	0.43	2.10
7.	K-14-7	6.50	1.55	1.40	76.80	0.75	0.44	2.71
8.	K-7-3A	7.70	1.25	1.20	76.67	0.91	0.38	2.05
9.	K-184	6.20	1.50	1.40	79.65	0.87	0.45	2.80
10.	P-60	6.16	1.74	1.20	76.68	0.79	0.42	2.61
11.	R-68-1-1	6.90	1.65	1.41	78.70	0.75	0.39	2.61
	Mean	7.16	1.47	1.16	78.21	0.84	0.42	2.53
	S. D.	0.54	0.16	0.16	1.35	0.06	0.04	0.44

* in grams per 16 grams of nitrogen.

TABLE 2—AMINO ACID COMPOSITION OF RICE

(grams per 16 grams of nitrogen)

No.	Variety	CYS	LYS	ASP	ALA	TRY	HIS	GLY	TYR	PHE	ARG	THR	PRO	VAL	ISO	SER	GLU	MET	LEU
1.	Jaya	1.72	4.70	6.97	4.54	0.78	2.08	5.46	2.75	4.55	7.54	3.90	5.72	4.55	5.11	4.62	18.85	1.82	7.05
2.	Satya	1.90	3.56	7.65	4.60	1.08	1.78	6.40	2.54	4.45	6.64	3.81	4.15	3.99	5.08	5.08	19.78	2.17	5.80
3.	Soorya	2.45	3.99	7.20	4.50	0.80	1.50	6.65	4.18	4.66	6.94	4.33	4.92	5.56	5.98	5.32	20.22	1.50	6.70
4.	Suhasini	2.57	4.02	7.58	5.11	0.60	1.58	7.84	3.36	2.74	7.94	4.20	4.12	4.90	5.25	4.97	22.40	1.96	7.35
5.	IR8	1.77	3.62	8.53	4.83	0.76	1.44	7.10	3.31	3.56	7.11	4.57	4.45	4.58	5.08	5.94	20.32	2.24	7.10
6.	TN_1	2.53	3.64	9.18	5.21	0.59	2.06	5.75	2.88	3.84	7.95	4.17	5.19	4.29	4.75	6.85	20.55	1.51	6.40
7.	K-14-7	2.25	4.30	10.13	4.90	0.90	1.66	7.50	3.15	5.25	8.70	4.50	4.62	5.76	5.70	6.60	22.50	2.10	7.43
8.	K-7-3A	1.81	4.05	7.02	4.80	0.78	1.95	6.37	2.73	4.10	6.79	4.29	4.55	4.55	5.20	5.72	19.50	2.12	6.55
9.	K-184	1.68	4.03	9.33	5.82	0.87	2.18	7.27	4.35	4.31	8.41	4.80	4.27	6.25	6.54	5.80	21.90	2.03	7.33
10.	P-60	1.72	3.99	8.10	5.70	1.02	1.64	7.25	3.49	3.83	8.43	4.61	6.53	4.78	6.50	5.60	21.81	1.55	7.40
11.	R-68-1-1	2.28	4.50	8.44	5.30	1.13	2.47	7.98	3.96	6.53	7.57	3.61	4.87	6.09	7.25	5.80	21.76	1.57	7.19
	Mean	2.06	3.64	8.20	5.03	0.85	1.85	6.87	3.61	4.40	7.64	4.25	4.85	5.25	5.68	5.65	20.87	1.85	6.94
	S. D.	0.34	0.55	0.97	0.46	0.17	0.33	0.79	0.59	0.84	0.69	0.35	0.70	0.72	0.69	0.63	1.00	0.29	0.52
	FAO[8]	2.0	4.2	—	—	1.4	2.4	—	—	2.8	2.0	2.8	—	4.2	4.2	—	—	2.2	4.8
	Eggum[9]	1.30	3.49	8.23	5.11	0.60	2.24	3.88	5.09	5.22	7.81	3.25	—	5.43	4.46	4.40	17.18	2.07	7.95

ABBREVIATIONS—

CYS—Cystine, LYS—Lysine, ASP—Aspartic acid,
ALA—Alanine, TRY—Tryptophan, HIS—Histidine,
GLY—Glycine, TYR—Tyrosine, PHE—Phenylalanine,
ARG—Arginine, THR—Threonine, PRO—Proline,
VAL—Valine, ISO—Isoleucine, SER—Serine,
GLU—Glutamic acid, MET—Methionine, LEU—Leucine.

TABLE 3 — ESSENTIAL AMINO ACID INDEX, BIOLOGICAL VALUE AND CHEMICAL SCORE OF RICE PROTEINS

No.	Variety	E.A.A.I.*	B.V.**	Chemical Score***
1.	Jaya	72.63	67.44	61.44
2.	Satya	70.52	65.17	50.86
3.	Soorya	74.94	69.58	57.01
4.	Suhasini	72.71	67.55	57.42
5.	IR8	70.78	65.45	51.71
6.	TN_1	68.42	62.88	52.00
7.	K-14-7	76.91	72.13	61.44
8.	K-7-3A	72.26	67.06	57.85
9.	K-184	82.56	78.29	57.57
10.	P-60	75.18	70.25	50.01
11.	R-68-1-1	85.53	81.52	64.28
	Mean	74.77	69.76	56.51
	S. D.	4.63	5.40	4.58

$$\text{*E.A.A.I.} = \sqrt[n]{\frac{Lys_p}{Lys_s} \times \frac{Try_p}{Try_s} \times \ldots\ldots \times \frac{His_p}{His_s}}$$

where p refers to food protein (rice protein), s is the std. protein (egg protein) and n is the number of amino acids viz. (1) Lysine, (2) Threonine, (3) Histidine, (4) Isoleucine, (5) Tryptophan, (6) Valine, (7) Leucine, (8) Arginine, (9) Methionine + Cystine and (10) Phenylalanine + Tyrosine.

**B.V. = 1.09 (E.A.A.I.) − 11.7.

***Chemical Score is the % of most limiting amino acid (Lysine) in the protein as compared to the requirement pattern given by Rama Rao et al.[12]

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Studies in the Oxidation of Propane 1 : 2 Diol by Acid Dichromate

UMA SHANKER and B. P. GYANI

Chemistry Department, Ranchi University, Ranchi 834 008

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AN attempt has been made to establish the steps in the oxidation of propane 1 : 2 diol by acid dichromate and the steps of reduction of dichromate in the same reaction potentiometrically. The diol loses 2, 4 and 6 electrons to give *stable* products (formaldehyde + acetaldehyde, formic acid and acetic acid). Formic acid is further oxidized to CO_2 only in strong sulphuric acid or in weaker acid (3N) after prolonged storage at room temperature (12-15 days).

The reduction of Cr(VI) to Cr(III) also takes place through steps of Cr(V) and Cr(IV). The latter reacts only slowly with the diol and is destroyed only after many hours.

Experimental

In these potentiometric 'titrations' we used 15.0 ml M/50 propane 1 : 2 diol in the cell and M/10 Cr(VI) in the burette. In reduction experiments the concentrations were interchanged. One would require 1.0 ml Cr(VI) to remove two electrons per molecule diol. In the reduction of $H_2Cr_2O_7 \rightarrow 2\ Cr(III)$ one would require 3.0 ml diol if the diol is oxidized to formic acid + acetic acid only. If the formic acid formd is oxidized to CO_2 and water the Cr(VI) requirement would be 4.0 ml.

We followed the potentials over long periods up to 20 days. The procedure is fully described in earlier papers[1,2].

Results and Discussion

Some of the results are given in Figs. 1 to 4. From our results we find that the diol (R) loses electrons one at a time in the following sequence,

$R \longrightarrow R_1 \longrightarrow R_2 \longrightarrow R_3 \longrightarrow$
diol — peroxy-diol — formaldehyde + acetaldehyde — peroxy-formaldehyde + acetaldehyde

$R_4 \longrightarrow R_5 \longrightarrow R_6 \longrightarrow R_7 \longrightarrow R_8$
formic acid + CH_3CHO — peroxy acetaldehyde + formic acid — acetic acid + formic ac. — peroxy formic ac. + acetic ac. — $CO_2 + H_2O$ + acetic ac.

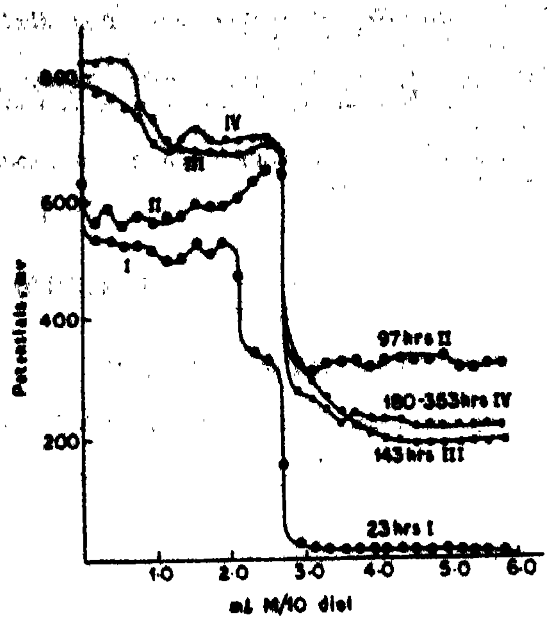


Fig. 1 3*N* Sulphuric acid

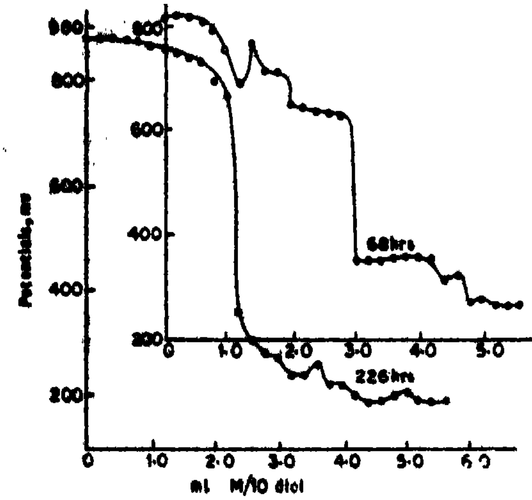


Fig. 2 6*N* Sulphuric acid

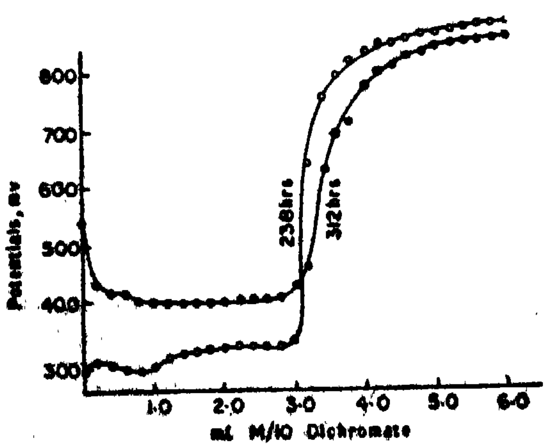


Fig. 3 3*N* Sulphuric acid

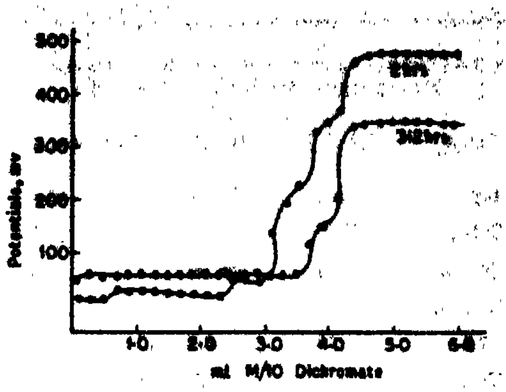


Fig. 4 5*N* Sulphuric acid

Inflexions corresponding to R_1, R_2, R_5, R_6, R_7 and R_8 have been observed but those corresponding to R_6 and R_7 last over many days. That for R_8 is permanent as expected. This means that there are only small periods of induction for futher oxidation after R_1, R_2 and R_5, perhaps none after R_3 and R_4 and quite long ones after R_6 and R_7.

The stable products have been identified chemically and spectrophotometrically. R_1, R_3, R_5 and R_7 correspond to formation of free radicals whose presence at these stages has been verified by induced polymerization of acrylonitrile to which the reagents were added in the right proportion at the right time.

In the reduction of acid dichromate by the diol again the indications are that Cr(VI) (P) gains electrons in steps of one in the following sequence

$$\underset{Cr(VI)}{P} \dashrightarrow \underset{Cr(V)}{P_1} \dashrightarrow \underset{Cr(IV)}{P_2} \dashrightarrow \underset{Cr(III)}{P_3} \dashrightarrow \underset{Cr(II)}{P_4}$$

Inflexions corresponding to the first three have been observed of which the P_2 stage lasts for many hours and P_3 is permanent. There is no observable reduction to Cr(II) (P_4), but a trace may perhaps be formed on prolonged storage with excess diol in 6*N* sulphuric acid to suppress the inflexion for Cr(III). These results show that at any stage in these reactions quite a number of oxidizing and reducing particles are involved. This situation has been ignored by some earlier workers [3,4] who have followed the reactions kinetically.

Acknowledgement

One of us (BPG) acknowledges financial support by the University Grants Commission.

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Concentration Dependence of Sedimentation Coefficient of Cellulose Trinitrate

B. DAS and A. K. RAY

Department of Applied Chemistry,
Calcutta University.

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SEDIMENTATION coefficients of macromolecules usually exhibit a pronounced dependence on the concentration of the solution. Although many attempts have been made to elucidate the reasons for such dependence and its relation to the properties of the macromolecules, our knowledge in this regard is still inadequate.

Various corrections have been proposed to obviate this difficulty. Lauffer[1] in a study on tobacco mosaic virus found that values of $S.\eta/\eta_0$ are constant within a fairly wide concentration range. From theoretical considerations also, it is expected that the macromolecules will behave in the same way. Jullander[2] has concluded that S_0 can be determined with reasonable accuracy for cellulose nitrates of molecular weight $1-2\times10^5$ by multiplying S with relative viscosity of the solution having 60% of the original concentration.

Burgers[3] proposed that the value of sedimentation coefficient at infinite dilution can be determined by extrapolating the data obtained at finite concentrations according to the equation

$$S=\frac{S_0}{1+kc} \quad (1)$$

$$\text{or,}\quad S=S_0(1-kc) \quad (2)$$

where S_0 is the sedimentation coefficient at infinite dilution, S the sedimentation coefficient at concentration c, and k a constant.

Newman[4] et al have employed the following relation for extrapolation of sedimentation coefficients to infinite dilution

$$S=S_0(1+k_s c+k'_s\, c^2)^{-1} \quad (3)$$

where k_s and k'_s are constants and c the concentration. This relation is essentially the same as the Burgers' equation except that it contains an additional term in concentration. The coefficients k_s and k'_s were readily determined graphically by a difference method according to the next relation which follows simply from equation (3)

$$\left(\frac{1}{S_2}-\frac{1}{S_1}\right)\Big/(c_2-c_1)=k_s+k'_s(c_2+c_1) \quad (4)$$

the subscripts 1 and 2 refer to any pair of data. This relation was found to represent the data very accurately. Following this, S_0 can be evaluated graphically from plots of $\left(\frac{1}{S}-k'_s c^2\right)$ vs. c.

The present investigation aims to examine the applicability of these extrapolation procedures for the determination of accurate S_0 values.

Experimental

Dry cellulose samples were treated with a mixture of phosphorous pentoxide and fuming nitric acid according to the method proposed by Alexander and Mitchell[5]. Cellulose trinitrate samples thus obtained were washed free of acid and thoroughly solvent exchanged with methanol and benzene, respectively. These were finally dried under vacuo. Sedimentation velocity experiments of the cellulose trinitrate samples in ethyl acetate and acetone were carried out in a Spinco model E analytical ultracentrifuge at a rotor speed of 44,770 rpm, using Schlieren optics. The boundary displacements were measured with a Comparator (Osaw, India) reading upto four decimals.

Relative viscosities at each concentration were determined using an Ubbelohde dilution viscometer at $30\pm0.1°$.

Results and Discussions

Values of $S_{20,w}$ are plotted against concentration in curve (1) of fig. 1. Samples of cellulose trinitrates, both in ethyl acetate and acetone, show a pronounced dependence on concentration. Corrections for relative viscosity were applied to these sedimentation coefficients and as can be seen, it resulted in an overcorrection for

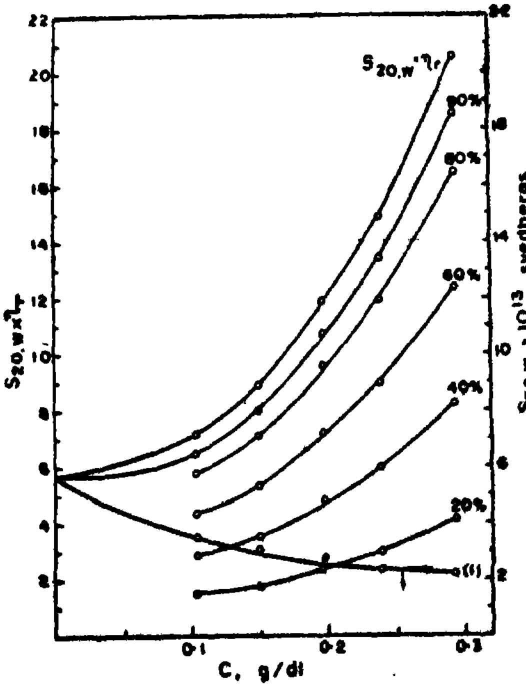


Fig. 1. Plot of $S_{20,w}$ vs. c & $\eta_r\times S_{20,w}$ vs c for Cellulose trinitrate in Acetone.

TABLE—1. SEDIMENTATION COEFFICIENT AND RELATIVE VISCOSITY OF CELLULOSE TRINITRATE IN ACETONE.

Concentration gms/dl.	$S_{20,w} \times 10^{13}$	$\eta_r = \eta/\eta_0$	$\frac{1}{S_{20,w}} - K'_s \times c^2$	$S_{20,w} \times C$	$S_{20,w} \times \eta_r$
0.2955	2.178	9.443	0.4614	0.6436	20.57
0.2396	2.392	6.200	0.4195	0.5732	14.84
0.1977	2.734	4.350	0.3668	0.5405	11.90
0.1508	3.054	2.886	0.3281	0.4606	8.81
0.1044	3.505	2.048	0.2856	0.3659	7.18

values at higher concentrations. However, at lower concentrations, the corrections were very low at the lower percentages of relative viscosities.

The Burgers' equation and the Newman-Loeb relation when applied to the present system, resulted in very good linear plots and the values obtained by extrapolation to infinite dilution were found to be in good agreement. The plots are shown in figs. (2) and (3).

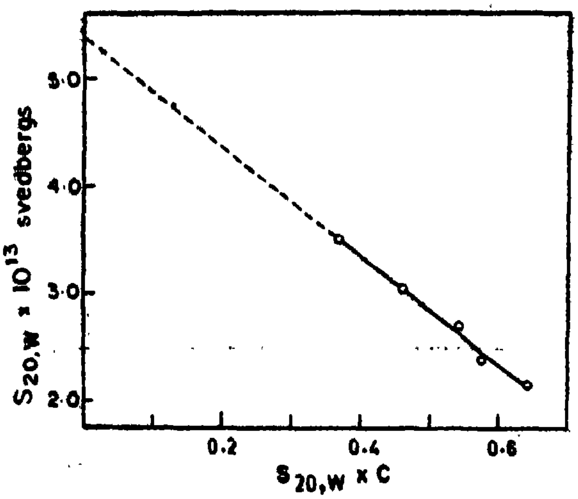


Fig. 2 Plot of $S_{20,w}$ vs $S_{20,w} \times c$ for Cellulose trinitrate in acetone.

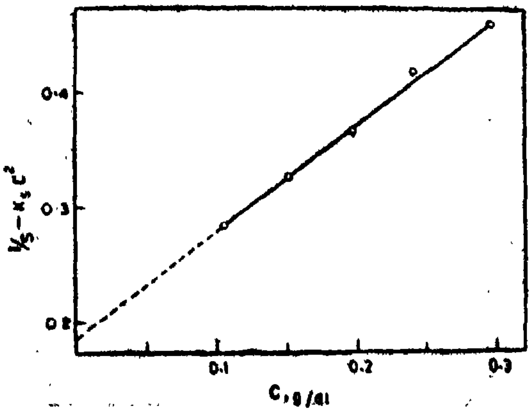


Fig. 3 Plot of $\left(\frac{1}{S} - K'_s\, c^2\right)$ vs c for Cellulose trinitrate in acetone.

TABLE—2. SEDIMENTATION COEFFICIENT AND RELATIVE VISCOSITY OF CELLULOSE TRINITRATE IN ETHYL ACETATE.

0.2180	2.178	9.642	0.4558	0.4749	21.00
0.1665	2.500	6.269	0.3981	0.4162	15.67
0.1396	2.756	4.737	0.3614	0.3847	13.05
0.1230	2.712	3.856	0.3676	0.3329	10.46
0.0786	3.251	2.327	0.3072	0.2555	7.56

The values of sedimentation coefficients obtained in ethyl acetate and acetone do not show a pronounced difference. It is expected that the sedimentation coefficient will depend on the viscosity of the medium, more resistance to the flow of the solute molecules will be offered in a medium in which the viscosity is higher. The data in tables 1 and 2 fulfil this expectation.

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Chemical Investigation of *Rumex dentatus* Linn

B. K. BHADORIA and R. K. GUPTA

Indian Grassland and Fodder Research Institute, Jhansi, U. P.

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RUMEX dentatus Linn. (Polygonaceae) commonly grows as an annual herb in Bundelkhand, gangetic plains and the sub-Himalayan tract upto 1000'. The plant is highly toxic to livestock causing diarrhoea and dermatitis[1-3]. No reference on its components is available in the literature, although, sister species[3-5]

have been chemically investigated. In view of the toxic nature of the plant, studies were undertaken on its chemical constituents and the presence of myricyl alcohol, β-D-glucoside of β-sitosterol, free β-sitosterol, emodin, aloe-emodin and quercetin is reported here.

Experimental

Powdered plant material (1.2 kg) was extracted with alcohol (95%) by percolation at room temperature. The alcoholic extractive was separated into petroleum ether (40-60°) and benzene soluble fractions. These fractions were chromatographed separately on Brockman's neutral alumina and silica-gel columns, respectively. Elution of the columns with different solvents and their mixtures yielded the following crystalline compounds.

Petroleum Ether extract :

Myricyl alcohol—Eluted with petroleum ether and crystallized from benzene, as colourless microcrystalline compound (260 mg), m.p. and mixed m.p. (with an authentic sample) 85° – 87°, $(\alpha)_D^{30°} \pm 0°$ ($CHCl_3$, *c* 1.3%) IR: ν_{max}^{KBr} 3460 cm^{-1} and formed a monoacetate m.p. 70-71°.

β-sitosterol—(Pet. ether: benzene, 1:1). It crystallised from acetone (charcoal) as colourless needles (650 mg) m.p. 136–37°, $(\alpha)_D^{30}$–33° ($CHCl_3$, *c* 1%) and showed positive tests for sterol: IR : ν_{max}^{KBr} 3420, 2920, 1470, 1370, 1055, 1030, 810 cm^{-1}. It formed an acetate m.p. 128-29° $(\alpha)_D^{30}$–37° ($CHCl_3$, *c* 1.2%) and was identified as β-sitosterol in the usual way.

β-D-glucoside of β-sitosterol δ : (ethyl acetate : ethanol : : 1:9). It crystallised from excess of ethanol (charcoal) as colourless crystalline product (430 mg) m.p. 270°–72°, IR : ν_{max}^{KBR} 3500, 2980, 2930, 1460, 1385, 1370, 1060 cm^{-1} and gave positive L-B and Molisch's tests. It formed an acetate (acetic anhydride and sodium acetate fused) m. p. 170°. On hydrolysis (alcoholic HCl 7%, 5 hr), it yieded β-sitosterol and glucose (paper co-chromatography) in two solvent systems butanol : acetic acid : water : : 4 : 1 : 5 and butanol : pyridine: water : : 3 : 1. 5 : 1 using aniline phthalate as detecting reagent). Mixed m.p. with authentic β-D-glucoside of β-sitosterol was not depressed.

Benzene extract :

Emodin—eluted with acetone and crystallised from ethanol as orange yellow needles (120 mg) m.p. 259-60°. It gave magenta colour with concentrated sulphuric acid and cherry red colour with aqueous alkali solution characteristic of emodin: IR : ν_{max}^{KBr} 3390, 2930, 1675, 1630, 1570, 1040, 768, 730 cm^{-1}. The compound was identified as emodin by its direct comparison with an authentic sample.

Aloe-emodin (acetone-alcohol, 1:1) was obtained as orange yellow crystalline product (65 mg) m.p. 222-23°.

Remaining alcoholic extractive was hydrolysed with alcoholic hydrochloric acid (7%, 3 hr). On extraction with ether, it gave a yellow product, which crystallised from acetone: methanol (1:1) mixture as yellow needles (170 mg) m.p. 310-312°. The compound answered tests for flavonols and formed an acetate (acetic anhydride and fused sodium acetate) m.p. 194-95°. Identity of the compound with quercetin was confirmed by paper chromatography in two solvent systems (butanol: acetic acid: water : : 4 : 1 : 5 and butanol saturated with water), mixed m.p. determination and spectral data.

Acknowledgement

The authors are grateful to Professor R.H. Thomson, Aberdeen University for very kindly providing authentic samples of emodin and aloe-emodin, to the Heads, PAR and WBC Divisions for facilities and to the Director, I.G.F.R.I., Jhansi for kind encouragement.

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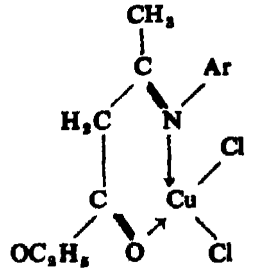
Complexes of Copper(II) with Ethyl-β-Arylaminocrotonates

A. C. DESAI and C. M. DESAI

P. T. Sarvajanik College of Science, Surat

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Ethyl-β-arylaminocrotonates are bidentate and get coordinated to copper from C=N nitrogen and C=O oxygen, the other two positions being linked to two halogens giving a six membered ring complex :



Such copper complexes are more stable towards water and sodium carbonate and have lower melting points when compared with zinc, cadmium and mercuric chloride complexes which decompose on air exposure[1] ; while the former darken on light exposure

TABLE—1

Ethyl-β-arylaminocrotonate $-CuCl_2$ complex	M. P. with Decomposition	Magnetic moment in B.M.	MW Rast's method Obser.	Calc.	% Chloride Found	Calc.	% Copper Found	Calc.	Molar conductance in mhos
1 ....anilino..	138–140°C	·1.54	385	339.5	20.79	20.91	18.61	18.71	16.64
2 ....2-methyl-anilino..	111–115°C	1.56	396	353.5	20.22	20.08	17.85	17.99	17.54
3 ....3-methyl-anilino..	119–121°C	1.55	392	353.5	20.16	20.08	17.76	17.99	17.96
4 ....4-methyl-anilino..	131–132°C	1.57	374	353.5	20.12	20.08	17.96	17.99	18.00
5 ....3-chloro-anilino..	152–153°C	1.50	405	373.9	18.82	18.99	16.79	16.94	17.78
6 ....4-chloro-anilino..	149–150°C	1.50	396	373.9	18.84	18.99	16.86	16.94	17.96

due to photo oxidation-reduction[2]. The spectrophotometric measurements using Job's method, mole ratio method and slope ratio method indicate the composition of the complexes as 1 : 1[3].

These complexes have been prepared by mixing equimolar (0.03*M*) alcoholic solutions of the chloride and the respective crotonate, when fine green crystals separated after half an hour. They are sparingly soluble in alcohol. Their magnetic moments were determined by using Guoy method and copper and chlorine by the usual methods. The analytical data are given in the table-1.

The low conductance values indicate their non-electrolytic nature and lower magnetic moment values have been attributed to dimerisation and some degree of dimerisation has been supported by molecular weight data ; such lowering in paramagnetism of Cu(II) complexes is known[4]. The probable structure of the complex is a square plane, copper(II) with d^9 configuration. The absorption spectrum in alcohol shows a broad band at 540 nm in agreement with D_{4h} symmetry of the Cu(II) complex.

Acknowledgement

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Dyes as Inhibitors for the Hydrogen Peroxide Decomposition

AJIT K. BANTHIA, SANKAR BISWAS and SANTI R. PALIT

Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032.

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HYDROGEN peroxide is a unique metabolite normally produced and destroyed by a wide variety of plants and animals[1]. Recently it has been suggested that cancer may originate by the action of an agent which directly or indirectly generates abnormally high concentration of H_2O_2 in the biological system[2]. Furthermore, the lethal function of the biological poisons, which are known to inhibit the decomposition of H_2O_2, can also be attributed to the increase of H_2O_2 concentration in excess of lethal doses[3]. As very many dyes are well known either as biological poisons or as carcinogens, it is worthwhile to study their effect on the acceleration[4] as also on the inhibition of H_2O_2 decomposition. In this preliminary note we report the inhibitory power of several groups of dyes viz. phthaleins, triphenyl methanes, thiazines etc.

Experimental

To have an idea of the inhibitory power of the dyes (listed in Table 1) we measured the rate of oxygen evolution from hydrogen peroxide solution both in the presence and absence of dyes under similar conditions and specially at the same *p*H (viz., *p*H 7) to avoid any *p*H effect. To verify the inhibitory power of the dyes from a different angle we measured the H_2O_2 concentration iodometrically in the original and final solutions. The changes in O.D values were determined by a Hilger U V speck spectrophotometer. It is evident from Table 1 that these dyes are very effective inhibitors for H_2O_2

decomposition. The order of the change in color of the dyes is: Malachite Green > Methyl Violet > Fluorescein > Floxine > Methylene Blue > Safranine > Auramine.

TABLE 1

Concentration of dye $= 1 \times 10^{-4} M$. Concentration of $H_2O_2 = 2.0(M)$ Temperature $= 35°C$; $pH = 7$

Sl No.	Dyes as inhibitors	Amt. of O_2 liberated in (c.c.) 1 day	Amt. of O_2 liberated in (c.c.) 7 days	Change in O.D value in 1 day	Change in O.D value in 7 days
1	Blank	3.5	55		
2	Malachite Green	0.0	0.5	Nil	90.6%
3	Auramine	0.0	1.0	,,	39.5%
4	Methyl Violet	0 0	1.2	,,	57.8%
5	Safranine	0.0	1.5	,,	40.0%
6	Methylene Blue	0.5	2.5	,,	61.7%
7	Floxine	1.0	6.0	,,	63.9%
8	Fluorescein	1 0	8.0	.	78.3%

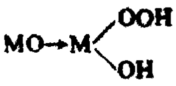
To have a clear idea of the inhibitory power of the dye Auramine, a short kinetic analysis was performed on the decomposition of H_2O_2. The experimental technique used involved the gas evolution method. The value of the rate constant (k) was determined from the slope of plot of -log $(V_\infty - V_t)$ vs. time t, where V_∞ and V_t are respectively the initial total volume of O_2 in the H_2O_2 solution and that liberated after the interval of a certain time t. Energy of activation (E_a) of the reaction was determined from the slope of the plot of log k vs 1/T, where T is the temperature (°k). The results obtained are given in Table 2. The large difference in k and E_a values between control and experimental samples illustrates well the high inhibitory power of Auramine.

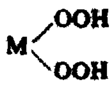
TABLE 2

Concn. of H_2O_2 (M)	Concn. of Auramine (M)	Temp. (°C)	k(Dye) $\times 10^7$	k(Blank) $\times 10^7$	E_a(Dye) kcal/mole	E_a(Blank) kcal/mole
		40	0.614	3.839		
4.0	3×10^{-4}	45	0.690	9.298	55.73	28.2
		50	0.776	17.60		

Results and Discussion

Mechanism: Stabilization of H_2O_2 by some metal oxides has been interpreted on the basis of the hypothesis that they are converted into hydrated peroxides as


or $MO_2.H_2O$, or possibly

$MO_2.H_2O_2$ or 

which are effective stabilising agents, and if the proportion of metal oxide to H_2O_2 is such as to lead to incomplete metal peroxide formation, there will be either feeble stabilization or a slight acceleration of the decomposition process[5]. Most of the dyes used in this work contain nitrogen in the chromophoric group. So the possibility of formation of hydrated amine peroxide complexes arises, as formation of such intermediate complexes in the production of N-amine oxide by the action of H_2O_2 on amine (both aliphatic and aromatic) is well known[6]. Thus a similar inhibition mechanism as described may occur. This idea is further corroborated by the observation that in dilute solution of H_2O_2, very little inhibition of H_2O_2 decomposition was envisaged. However, we could not get any spectrophotometric evidence of such complex formation in our preliminary investigations. Still it is interesting to note that a dye retains its inhibition power strongly even after nearly complete fading of its color after seven days (Table 1). Interestingly enough, we might also be tempted to correlate the fading of color in the dyes (where N forms the chromophoric group) with the formation of amine peroxide complexes thereby destroying the chromophoric N. In the other dyes where there is no nitrogen in the chromophore e.g. in the case of floxine and fluorescein, there is a quinone structure capable of impeding the free radical decomposition process of H_2O_2. Incidentally they are the least active inhibitors of the dyes studied (Table 1).

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Studies in the synthesis of Quinoline Derivatives Part VIII**. Synthesis of 4 : 3′-methylenebis-(2,2′-dichloro-4′-methylquinoline) Derivatives

P. V. THAKORE and K. N. TRIVEDI*

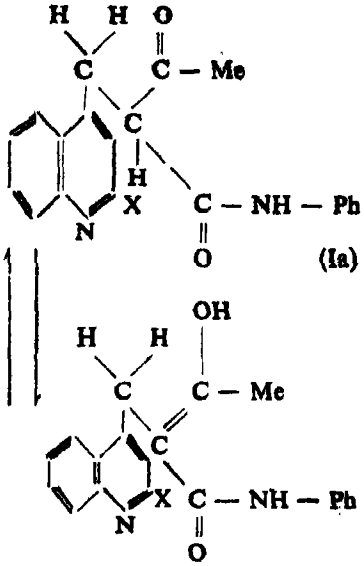
Chemistry Department, Faculty of Science,
M. S. University of Baroda,
Baroda-390 002

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IN continuation of our work on reactivity of 4-Bromomethyl-2-hydroxy and 4-Chloromethyl-2-chloroquinoline derivatives[1,2,3], we report here the condensation of 4-chloromethyl-2-chloroquinoline and 4-bromomethyl-2-hydroxyquinoline with sodium salt of acetoacetanilide in the presence of Dimethyl sulphoxide, to give α-2-chlorolepidinyl acetoacetanilide (Ia) and α-2-hydroxylepidinyl acetoacetanilide (Ib), respectively. It was observed that the condensation did not occur in the absence of DMSO. The structure of (Ia) was confirmed by NMR spectrum (DMSO-d_6+acetone-d_6), δ, 2.3, singlet, 3H, for methyl group ; 3.65, doublet, J=8Hz , 2H, for $-CH_2$-group ; 4.25, triplet, J=8Hz , 1H, for -CH-group ; 3.25, singlet, 1H, for -NH-group, which disappears on D_2O-exchange ; 7.1 to 8.0, multiplet 9H, aromatic protons. It also shows the enolic proton at δ, 10.6 which disappears on D_2O-exchange, indicating that it partially exists in the enolic form (Ic). The lower value obtained for the methylene protons at δ, 3.65, in the spectrum is due to the additional deshielding effect of the carbonyl group as shown in the structure (Ia). On the basis of integration values of methyl, methylene and enolic protons, it is calculated that the percentage of enol content is 20%. This is supported by the IR of (Ia) which shows broad enolic band at 3250 cm^{-1} and broad ketonic band of enol at 1570 cm^{-1}. (Ia) and (Ib) underwent cyclization when reacted with conc. H_2SO_4 to give 4 : 3′-methylenebis-(2-chloro-2′-hydroxy-4′-methylquinoline) (IIa) and 4 : 3′-methylenebis-(2,2′-dihydroxy-4′-methylquinoline) (IIb) respectively. (IIa) and (IIb) when reacted with phosphorous oxychloride, gave the same 4 : 3′-methylenebis-(2,2′-dichloro-4′-methylquinoline), (IIc). The structure of (IIc) is also confirmed by NMR spectrum ($CDCl_3$), δ, 2.6, singlet. 3H, $-CH_3$-group , 4.8, singlet, 2H, $-CH_2$-group ; 6.6, singlet, 1H, aromatic proton of quinoline ring at 3-position, 7.3 to 8.2, multiplet 8H, for aromatic protons.

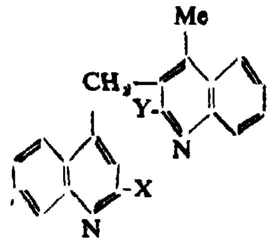
Experimental

General method for the synthesis of α-2-chlorolepidinylacetoacetanilides : Pulverised sodium (0.23 g.) in dry benzene, was added acetoacetanilide (1.77 g.) and the mixture was refluxed for 5-6 hr. on water bath. 4-chloromethyl-2-chloroquinoline (2.2 g.) and Dimethyl sulphoxide (2.0 ml.) were added to the above reaction mixture. The whole reaction mixture was refluxed for 8-9 hrs. The reaction mixture was poured in water, the residue filtered off and washed with water and finally crystallized from benzene. The m. ps. and the analytical data are reported in Table 1. The yields of products varied from 70 – 80%.



(Ia) X = Cl

(Ib) X = OH



(IIa) X = Cl, Y = OH

(IIb) X = Y = OH

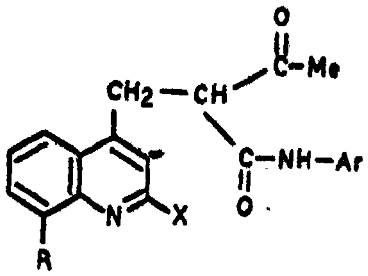
(IIc) X = Y = Cl

4 : 3′-Methylenebis-(2-chloro-2′-hydroxy-4′-methylquinoline) derivatives (IIa) : α-2-Chlorolepidinylacetoacetanilide (3.5g.) was dissolved in conc. H_2SO_4 (5.0 ml.) and heated for 90 min. at 80-90° on water bath. The reaction mixture was poured on crushed ice, the residue was filtered off and crystallized from acetic acid. The m. ps. and the analytical data are reported in Table 2. The yields of products varied from 70-80%.

4 : 3′-Methylenebis-(2,2′-dichloro-4′-methylquinoline) derivatives (IIc) : The above (IIa), (1.0 g.) was heated with phosphorus oxychloride (3.0 g.) on an oil-bath at 110-15° for 2 hrs. The reaction mixture was cooled and poured on crushed ice and the products crystallized from benzene. The m. ps. and analytical data are reported in Table 2. The yields of products varied from 40-50%.

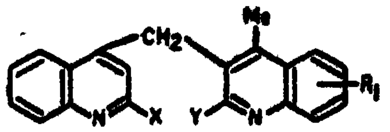
**R. J. CHUDGAR and K. N. TRIVEDI, *J. Indian Chem. Soc.*, 1972, 49, 49 (for the previous part VII).

TABLE I



Ar	R	X	m.p.	Found % C	Found % H	Found % N	Found % Cl	Molecular Formula	Required % C	Required % H	Required % N	Required % Cl
Ph	H	Cl	157	68.58	5.05	7.48	10.00	$C_{20}H_{17}N_2O_2Cl$	68.10	4.82	7.94	10.08
Ph	H	OH	265	71.52	5.21	7.94	—	$C_{20}H_{18}N_2O_3$	71.86	5.39	8.39	—
o-MeC_6H_4	H	Cl	199	68.36	5.48	7.15	10.10	$C_{21}H_{19}N_2O_2Cl$	69.75	5.18	7.64	9.68
o-$MeOC_6H_4$	H	Cl	178	65.95	4.91	7.76	9.17	$C_{21}H_{19}N_2O_3Cl$	65.88	4.96	7.32	9.28
p-$MeOC_6H_4$	H	Cl	189	65.73	5.11	7.80	9.00	$C_{21}H_{19}N_2O_3Cl$	65.88	4.96	7.32	9.28
p-$MeOC_6H_4$	H	OH	240	69.64	5.49	7.84	—	$C_{21}H_{20}N_2O_4$	69.23	5.49	7.69	—
m-ClC_6H_4	H	Cl	166	61.70	4.54	7.71	18.55	$C_{20}H_{16}N_2O_2Cl_2$	62.01	4.13	7.23	18.35
m-ClC_6H_4	H	OH	233	65.06	5.02	7.29	10.00	$C_{20}H_{17}N_2O_3Cl$	65.13	4.61	7.60	9.63
p-ClC_6H_4	H	Cl	185	61.90	4.53	7.06	17.29	$C_{20}H_{16}N_2O_2Cl_2$	62.01	4.13	7.23	18.35
p-ClC_6H_4	H	OH	265	64.90	4.84	7.26	9.55	$C_{20}H_{17}N_2O_3Cl$	65.13	4.61	7.60	9.64
p-Br_6H_4	H	Cl	187	55.37	3.57	6.44	—	$C_{20}H_{16}N_2O_2BrCl$	55.61	3.70	6.49	—
α-$C_{10}H_7$	H	Cl	200	72.05	4.99	6.92	8.54	$C_{24}H_{19}N_2O_2Cl$	71.57	4.72	6.96	8.82
α-$C_{10}H_7$	H	OH	280	74.82	5.34	7.09	—	$C_{24}H_{20}N_2O_3$	75.00	5.21	7.29	—
Ph	CH_3	OH	242	72.05	5.62	7.99	—	$C_{21}H_{20}N_2O_3$	72.42	5.74	8.05	—
Ph	CH_3	Cl	135	68.54	5.45	7.52	10.09	$C_{21}H_{19}N_2Cl$	68.75	5.18	7.64	9.68
o-MeC_6H_4	CH_3	Cl	195	69.18	5.12	7.32	9.55	$C_{22}H_{21}N_2O_2Cl$	69.38	5.52	7.36	9.33
o-MeC_6H_4	CH_3	OH	274	72.69	6.26	6.98	—	$C_{22}H_{22}N_2O_3$	72.94	6.08	7.74	—

TABLE 2



R_1	R	X	Y	m. p.	Found % C	Found % H	Found % N	Found % Cl	Molecular formula	Required % C	Required % H	Required % N	Required % Cl
H	H	OH	OH	>360	75.56	5.18	8.22	—	$C_{20}H_{14}N_2O_2$	75.96	5.06	8.85	—
H	H	Cl	OH	300	71.30	4.47	8.32	10.93	$C_{20}H_{15}N_2OCl$	71.76	4.48	8.37	10.62
H	H	Cl	Cl	210	68.06	3.82	7.89	20.56	$C_{20}H_{14}N_2Cl_2$	68.00	3.96	7.93	20.11
6-MeO	H	OH	OH	>360	72.38	4.98	7.91	—	$C_{21}H_{18}N_2O_3$	72.84	5.20	8.09	—
6-MeO	H	Cl	OH	291	68.89	5.07	7.32	9.51	$C_{21}H_{17}N_2O_2Cl$	69.13	4.66	7.68	9.47
8-MeO	H	Cl	OH	296	69.63	4.58	8,01	9.39	$C_{21}H_{17}N_2O_2Cl$	69.13	4.66	7.68	9.74
7-Cl	H	OH	OH	>360	68.69	4.04	7.64	10.50	$C_{20}H_{15}N_2O_2Cl$	68.47	4.28	7.99	10.13
7-Cl	H	Cl	OH	315	64.87	4.41	7.84	19.70	$C_{20}H_{14}N_2OCl_2$	65.05	3.79	7.59	19.20
7-Cl	H	Cl	Cl	249	61.51	3.55	7.25	27.10	$C_{20}H_{13}N_2Cl_3$	61.93	3.35	7.23	27.47
6-Cl	H	OH	OH	>330	68.60	4.56	7.59	10.56	$C_{20}H_{15}N_2O_2Cl$	68.47	4.28	7.99	10.13
H	CH_3	OH	OH	>360	73.77	5.49	8.19	—	$C_{21}H_{18}N_2O_2$	73.37	5.45	8.49	—
H	CH_3	Cl	Cl	228	68.72	4.68	7.88	19.55	$C_{21}H_{16}N_2Cl_2$	68.66	4.36	7.63	19.35
8-Me	CH_3	OH	OH	>360	76.35	5.65	8.00	—	$C_{22}H_{20}N_2O_2$	76.74	5.81	8.14	—
8-Me	CH_3	Cl	Cl	205	69.08	4.60	7.87	18.55	$C_{22}H_{18}N_2Cl_2$	69.30	4.73	7.35	18.64
Benzo (h)	H	OH	OH	>360	79.01	5.10	7.82	—	$C_{24}H_{18}N_2O_2$	78.69	4.92	7.65	—
Benzo (h)	H	Cl	OH	>360	75.08	4.63	7.16	9.50	$C_{24}H_{17}N_2OCl$	74.90	4.42	7.28	9.23
Benzo (h)	H	Cl	Cl	271	71.74	4.23	6.92	17.55	$C_{24}H_{16}N_2Cl_2$	71.46	3.97	6.95	17.62

Acknowledgement

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3. C. S. GARNER and D. A. HOUSE in "Transition Metal Chemistry", (Ed.) R. L. CARLIN, Marcel Dekker, New York, 1970, vol 6, p. 59.

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